Surface modification of Coal Fly Ash by Sodium Lauryl Sulphate

By

Confidence Lethabo Mathebula

Submitted in partial fulfilment of the degree

MAGISTER SCIENTIAE

In the Faculty of Natural and Agricultural Sciences

UNIVERSITY OF PRETORIA
PRETORIA

Supervisor: Dr E.M van der Merwe

February 2013

© University of Pretoria
DECLARATION

I Confidence Lethabo Mathebula declare that the dissertation, which I hereby submit for the degree of Magister Scientiae at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at another university.

........................................
SIGNATURE

........................................
DATE
ACKNOWLEDGEMENTS

- **Dr E.M van der Merwe** (Supervisor) – For being more than just a supervisor but a friend as well and for allowing me to be part of your life. Thank you for the best 3 years of post-graduate studies

- **Dr L.C Prinsloo** (Co-Supervisor) – For your helpful input and smile every time I came to ask for your help.

- **Ma, Naidah Mathebula** – I know that when you finally read this you will be speechless, Thank you for being my rock. Love you so much.

- **Grandpa, Elson Mathebula** – This journey started with you, I’m thankful that you are still in it with me.

- **Prof van Rooyen and Prof Vleggar** – Thank you for the big round bottom flasks and the heating mantle

- **Mr Allan Hall and Mr C. van der Merwe** from the Department of Microscopy – For their availability and help with SEM and TEM

- **Mr Bernard Reeksting** from Polymer Science at CSIR - For his valued and appreciated help with filler and polymer science

- **Miss Nontete** – For her help with TGA-FTIR analysis and interpretation, thank you dear

- **Dr RA Kruger** – For his expertise in fly ash

- **Impala Platinum** (Bursaries and Processing Laboratories) – For allowing me an extra year to continue with my studies, thank you.

- **MTV (L) [Mboni, Thandi, Van and Me]** – You are the craziest bunch that I know and that is the just what I needed and I appreciate each of you. What’s next ladies

- **My Family ELIM Full Gospel Church** – Thank you for accepting and loving me as I am, and for all your support and prayers. I miss you all.

- **Friend and Family** – Thank you for being there and for all the support, much appreciated

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.
Let no one despise you for your youth, but set the believers an example in speech, in conduct, in love, in faith, in purity

1 Timothy 4:12

Rejoice always, pray continually, give thanks in all circumstances; for this is God's will for you in Christ Jesus

1 Thessalonians 5:16-18
SUMMARY

Thirty million tons of coal fly ash are produced each year in South Africa of which approximately 5% is utilised beneficially. With the growing concern about pollution and increasing landfill costs, the study of the utilisation and application of coal fly ash has increased worldwide.

The morphology and particle size of fly ash make it suitable for application as filler in polymers, but its application is hindered by the lack of compatibility between the inorganic surface of the ash and the organic matrix of the polymer. Another concern is the agglomeration between fly ash particles. For this reasons, surface treatment is usually performed on mineral fillers to enhance workability and compatibility between the polymer and filler.

This study involved the surface modification of South African coal fly ash with an anionic surfactant, sodium lauryl sulphate (SLS), under different treatment conditions. Surface and physical properties of the untreated and treated fly ash were studied systematically by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in order to determine the extent of interaction between the SLS and the fly ash surface. Other analytical techniques applied include Thermogravimetric analysis (TGA-FTIR), Particle size distribution, X-ray diffraction (XRD) and X-ray fluorescence spectroscopy (XRF), Raman spectroscopy and Fourier Transform Infrared spectroscopy (FTIR).

Although the overall chemical composition of the SLS modified coal fly ash investigated in this study was not altered extensively, significant changes could be observed in its physical properties. The hydrophilic surface of untreated fly ash was rendered hydrophobic after SLS treatment. SEM results indicated a decrease in agglomeration between fly ash spheres upon surfactant treatment, while results obtained from TEM have shown agglomerates on the surface of most of the fly ash spheres. There is a distinct difference between the morphology of agglomerates on the untreated and SLS modified fly ash, and also between samples treated under different conditions. Not all SLS modified fly ash particles were covered with agglomerates to the same degree.

Results obtained from FTIR and TGA-FTIR studies were promising in the sense that hydrocarbon fractions could be observed in the TGA-FTIR decomposition products. The possibility of interactions between fly ash and SLS could be deduced from the FTIR results of the solid samples, due to a small shift in peak positions of the S-O stretch vibration, which may
be indicative of electrostatic interactions rather than bonding interactions between SLS and fly ash. The presence of SLS could not be confirmed by Raman spectroscopy, but rendered information about the spatial distribution of the various phases in the fly ash.

Feasibility tests were performed on the application of fly ash samples as filler in PVC. These results indicate that SLS treated fly ash can successfully replace CaCO$_3$ as filler in PVC under conditions of low filler loadings.
# TABLE OF CONTENTS

DECLARATION ..................................................................................................................... i  
ACKNOWLEDGEMENTS ..................................................................................................... ii  
SUMMARY ........................................................................................................................... iv  
LIST OF ABBREVIATIONS ................................................................................................ xi  
LIST OF FIGURES .............................................................................................................. xii  
LIST OF TABLES ............................................................................................................... xvi

CHAPTER 1 ........................................................................................................................... 1  
INTRODUCTION .................................................................................................................. 1
  1.1 Background ...................................................................................................................... 1
  1.2 Fly ash ........................................................................................................................... 2
    1.2.1 Utilisation of fly ash .................................................................................................. 3
        a. Cement and concrete ............................................................................................... 4
        b. Soil ameliorant ......................................................................................................... 5
        c. Wastewater Treatment ............................................................................................ 5
        d. Toxic waste Treatment ............................................................................................ 6
        e. Mine Backfill .......................................................................................................... 6
        f. Mullite and glass ceramics production .................................................................... 6
        g. Inorganic Filler into Polymers ................................................................................ 7
  1.3 Surfactants .................................................................................................................... 8
    1.3.1 Cationic surfactants ............................................................................................... 9
    1.3.2 Anionic surfactants .............................................................................................. 10
    1.3.3 Critical Micelle Concentration (c.m.c) ................................................................ 11
    1.3.4 Mechanism of surface surfactant adsorption ....................................................... 12
    1.3.5 Counter ion effect on surfactant aggregation ....................................................... 14
  1.4 Study Objective .......................................................................................................... 15
  1.5 Reference ..................................................................................................................... 16
CHAPTER 2 ......................................................................................................................... 20
THEORETICAL DESCRIPTION OF ANALYTICAL TECHNIQUES ........................................... 20

2.1 X-ray Powder Diffraction (XRD) ........................................................................................ 20
2.2 X-ray Fluorescence (XRF) .................................................................................................. 21
2.3 Raman and Infrared spectroscopy ...................................................................................... 22
  2.3.1 Infrared (IR) Spectroscopy .......................................................................................... 23
  2.3.2 Raman Spectroscopy .................................................................................................. 24
2.4 Thermogravimetric analysis (TGA-FTIR) .......................................................................... 25
2.5 Scanning Electron Microscopy (SEM) ................................................................................ 26
2.6 Transition Electron Microscopy (TEM) ............................................................................. 28
2.7 Particle Size distribution ..................................................................................................... 29
2.8 References .......................................................................................................................... 30

CHAPTER 3 ......................................................................................................................... 33
EXPERIMENTAL .................................................................................................................. 33

3.1 Materials ............................................................................................................................ 33
3.2 Coal Fly Ash modification .................................................................................................. 33
3.3 Characterisation techniques .............................................................................................. 34
  3.3.1 X-ray Diffraction (XRD) .......................................................................................... 34
  3.3.2 X-ray Fluorescence (XRF) ....................................................................................... 35
  3.3.3 FTIR spectroscopy .................................................................................................... 35
  3.3.4 Raman spectroscopy .................................................................................................. 36
  3.3.5 Thermogravimetric analysis (TGA-FTIR) .................................................................. 37
  3.3.6 Scanning Electron Microscopy (SEM) ...................................................................... 37
  3.3.7 Transmission Electron Microscopy (TEM) ................................................................. 38
  3.3.8 Particle size ................................................................................................................ 39
3.4 References .......................................................................................................................... 40
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abr</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>c.m.c</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>Calcium Carbonate</td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium Oxide</td>
</tr>
<tr>
<td>cm$^{-1}$</td>
<td>Wavenumber</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>FA</td>
<td>Fly Ash</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>g/cm$^3$</td>
<td>grams per cubic centimetre</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric Acid</td>
</tr>
<tr>
<td>hrs</td>
<td>Hours</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>KB</td>
<td>Kulucoite</td>
</tr>
<tr>
<td>KBr</td>
<td>Potassium Bromide</td>
</tr>
<tr>
<td>KC</td>
<td>Kulubrite</td>
</tr>
<tr>
<td>KIO$_3$</td>
<td>Potassium Iodate</td>
</tr>
<tr>
<td>M</td>
<td>Molar</td>
</tr>
<tr>
<td>MD</td>
<td>Milling Direction</td>
</tr>
<tr>
<td>MPa</td>
<td>Megapascal</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>Pb</td>
<td>Lead</td>
</tr>
<tr>
<td>Phr</td>
<td>Parts per hundred resin</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle Size Distribution</td>
</tr>
<tr>
<td>PVA</td>
<td>Polyvinyl Alcohol</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl Chloride</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SLS</td>
<td>Sodium Lauryl Sulphate</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TFA</td>
<td>Treated Fly Ash</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TV</td>
<td>Transverse Direction</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1. 1: Sample of raw fly ash ................................................................................................ 2

Figure 1. 2: Spherical nature of fly ash particles observed under a scanning electron microscope ................................................................................................................................ 7

Figure 1. 3: Surfactant classification according to the charge of their head group .................8

Figure 1. 4: Example of a Cationic Surfactant, Trimethylhexadecyl Ammonium Chloride ......10

Figure 1. 5: Example of an Anionic Surfactant, Sodium dodecylbenzenesulphonate ...........10

Figure 1. 6: Representation of a spherical micelle [Domínguez, 1997] ................................. 11

Figure 1. 7: The four region model of surfactant adsorption as from Atkin 2003 (a) .............13

Figure 1. 8: The two-step model of surfactant adsorption as taken from Atkin 2003 (a) The
regions presented in the figure are (I) a low surface excess region, (II) the first plateau region,
(III) a hydrophobic interaction region and (IV) the second plateau. ........................................ 14

Figure 2. 1: Diffraction of X-rays by a crystalline substance ............................................ 21

Figure 2. 2: Principles of X-ray Fluorescence ..................................................................... 22

Figure 2. 3: Example of stretching and bending vibrations of a water molecule ............. 24

Figure 2. 4: Illustration of fluorescence, infrared absorption and Raman scattering (Rayleigh,
Stokes and anti-Stokes) ............................................................................................................... 25

Figure 3. 1: PANalytical X’Pert Pro powder diffractometer ........................................... 34

Figure 3. 2: ARL 9400XP ................................................................................................. 35

Figure 3. 3: The Bruker 70v Fourier Transform Infrared (FTIR) spectrometer with microscope
attachment (left) and the TX6400 Raman spectrometer (right) ............................................ 36

Figure 3. 4: View of fly ash particles under the Raman microscope with 50x (left) magnification and 100x magnification (right) .......................................................... 36

Figure 3. 5: Perkin Elmer TGA 4000 FTIR ..................................................................... 37

Figure 3. 6: JEOL JSM 840 Scanning Electron Microscope (SEM) .................................. 38

Figure 3. 7: JEOL JEM 2100F TEM ............................................................................. 38

Figure 3. 8: Malvern Mastersizer 2000 ........................................................................... 39
Figure 4.1: XRD spectrum of untreated fly ash ................................................................. 42
Figure 4.2: The silica-oxygen framework of a glass ....................................................... 43
Figure 4.3: SEM micrographs of untreated Lethabo coal fly ash ................................. 45
Figure 4.4: TEM micrograph of untreated Lethabo coal fly ash ................................. 45
Figure 4.5: FTIR transmission spectrum of untreated fly ash ...................................... 47
Figure 4.6: FTIR spectra of glass (bottom) and quartz (top) ........................................... 48
Figure 4.7: FTIR reflectance spectrum of untreated fly ash ........................................... 49
Figure 4.8: Raman spectra of untreated fly ash at different analysis points .................. 50
Figure 4.9: Raman spectra of untreated fly ash at different analysis points ................. 52
Figure 4.10: TGA-FTIR results obtained for the untreated Lethabo fly ash ............... 53
Figure 4.11: Particle size distribution of untreated Lethabo fly ash ......................... 54

Figure 5.1: Chemical and structural formula of Sodium Lauryl Sulphate .................. 58
Figure 5.2: XRD spectrum of 2.0% SLS treated fly ash sample treated for 18 hours at 80 °C .. 60
Figure 5.3: SEM monograms of untreated and SLS treated fly ash ............................ 62
Figure 5.4: SLS treated fly ash samples for 6 hours at 80 °C ....................................... 63
Figure 5.5: 2.0% SLS treated fly ash samples at 80 °C and different exposure periods .... 64
Figure 5.6: 2.0% SLS treated fly ash samples at 50 and 80 °C for 6 hours ..................... 65
Figure 5.7: Comparison of the lognormal size distributions of untreated fly ash, and samples treated in distilled water and SLS for 6 hours at 80 °C ............................................................... 65
Figure 5.8: Comparison of the lognormal size distributions of untreated fly ash, and samples treated in distilled water and SLS for 66 hours at 80 °C ............................................................. 66
Figure 5.9: FTIR spectrum of Sodium Lauryl Sulphate ................................................. 68
Figure 5.10: Raman spectrum of Pure SLS taken at two wavenumber ranges ............ 68
Figure 5.11: FTIR spectra of treated FA samples at 50 °C for 18 hours, untreated FA and pure SLS .................................................................................................................. 69
Figure 5.12: FTIR spectra of treated FA samples at 80 °C for 18 hours, untreated FA and pure SLS .................................................................................................................. 70
Figure 5.13: FTIR spectra of treated FA samples at 50 °C for 6 hours, untreated FA and pure SLS.

Figure 5.14: FTIR spectra of treated FA samples at 80 °C for 6 hours, untreated FA and pure SLS.

Figure 5.15: Comparison of FTIR spectra of pure SLS, untreated fly ash, and 2.0% SLS treated fly ash for 6 hours at 80 °C.

Figure 5.16: The different Raman spectra of 2.0% SLS treated fly ash at 80 °C for 6 hours obtained during 2D scanning of a small area of flyash.

Figure 5.17: Raman spectra of 2.0% SLS treated fly ash at 80 °C for 6 hours using different analysis sites shown.

Figure 5.18: Comparison of Raman spectra of pure SLS and 2.0% SLS treated fly ash for 6 hours at 80 °C.

Figure 5.19: TEM image of fly ash treated for 18 hours in distilled water at 50 °C.

Figure 5.20: TEM images of treated Lethabo fly ash for 6 hours at 80 °C.

Figure 5.21: TGA-FTIR results obtained for SLS Powder.

Figure 5.22: TGA-FTIR results obtained for the 2.0% SLS treated fly ash, at 80 °C for 6h.

Figure 5.23: Photographs of water droplets deposited on surfaces of a fly ash powder bed, taken 1 s after deposition.

Figure 6.1: SEM images of fly ash samples treated at 80 °C for 6 hours.

Figure 6.2: SEM images of fly ash samples treated at 80 °C for 6 hours.

Figure 6.3: SEM images of fly ash samples treated at 80°C for 6 hours.

Figure 6.4: TEM images of fly ash samples treated at 80 °C for 6 hours KIO₃-Surfactant solution.

Figure 6.5: TEM images of fly ash samples treated at 80 °C for 6 hours with NaCl-Surfactant solution.

Figure 6.6: FTIR spectra of fly ash samples treated at 80 °C for 6 hours with KIO₃-SLS.

Figure 6.7: Raman spectra of 2.0% SLS-0.1 M KIO₃ treated fly ash at 80 °C for 6 hours at different analysis sites shown.

Figure 6.8: FTIR spectra of fly ash samples treated at 80 °C for 6 hours with NaCl-SLS.

Figure 6.9: Raman spectra of 2.0% SLS-0.1 M NaCl treated fly ash at 80 °C for 6 hours at different analysis sites shown.
Figure 7.1: Reflux system for surfactant treatment on fly ash.................................93
Figure 7.2: SEM images of refluxed fly ash samples treated for 6 hours.........................94
Figure 7.3: SEM images of SLS refluxed fly ash samples at higher magnifications, showing surface coating .................................................................95
Figure 7.4: TEM images of 2.0% SLS refluxed fly ash samples........................................95
Figure 7.5: TEM images of 4.0% SLS refluxed fly ash samples........................................96
Figure 7.6: FTIR spectra of refluxed fly ash samples treated for 6 hours .........................96
Figure 7.7: Raman spectra of 4.0% SLS reflux treated fly ash for 6 hours taken at different analysis sites shown .................................................................97
Figure 7.8: TGA-FTIR results obtained for the 4.0 % SLS refluxed fly ash treated for 6hrs ...98
Figure 7.9: Photographs of water droplets deposited on surfaces of a fly ash powder bed, taken 1 s after deposition ........................................................................99

Figure 8.1: Comparison of the elongation at break of untreated fly ash (FA), treated fly ash (TFA), kulubrite 2 (KB) and kulucote 2 (KC) filled PVC formulations along milling direction .................................................................105
Figure 8.2: Comparison of the tensile strength of untreated fly ash (FA), treated fly ash (TFA), kulubrite 2 (KB) and kulucote 2 (KC) filled PVC composites along milling direction ..............105
Figure 8.3: Comparison of the elongation at break of untreated fly ash (FA), treated fly ash (TFA), kulubrite 2 (KB) and kulucote 2 (KC) filled PVC composites in transverse direction 107
Figure 8.4: Comparison of the tensile strength of untreated fly ash (FA), treated fly ash (TFA), kulubrite 2 (KB) and kulucote 2 (KC) filled PVC composites in transverse direction ............107
Figure 8.5: SEM micrographs of the fracture surface of untreated fly ash samples and PVC formulation for the different amounts of filler added ..........................................................108
Figure 8.6: SEM micrographs of the fracture surface of SLS treated fly ash samples and PVC formulation for the different amounts of filler added ..........................................................109
Figure 8.7: SEM micrographs of the CaCO\textsubscript{3} and PVC formulation for 30 phr ........109
LIST OF TABLES

Table 4.1: Quantitative XRD results of untreated Lethabo fly ash.................................43
Table 4.2: XRF chemical composition of Lethabo fly ash (Class F)...............................44
Table 4.3: The FTIR wavenumber assignment of silicate species as well as other compounds that were found in the analysed fly ash sample. .........................................................46
Table 4.4: Main peaks in Raman spectra of components found in fly ash [Voll, 2002; and Schneider, 2005] .........................................................................................................................49

Table 5.1: XRD quantitative results of untreated fly ash (FA) and 2.0% SLS treated fly ash sample at 80 °C for 18 hours (18hrs SLS) values are reported as weight percentage ..........59
Table 5.2: XRF chemical composition of untreated fly ash (FA) and of 2.0% SLS treated fly ash sample at 80 °C for 6 hours (6 h SLS), values are reported as weight percentage ..........61
Table 5.3: Assignment of FTIR and Raman Frequencies for SLS [Larkin, 2011] .................67

Table 6.1: XRF chemical composition of untreated fly ash (FA), KIO_3-SLS and NaCl-SLS treated fly ash for 6 hours; values are reported as weight percentages .........................84

Table 8.1: Materials used for the formation of PVC formulation .....................................102
Table 8.2: Relative densities of filled PVC composites ......................................................103
Table 8.3: Mechanical properties of untreated and treated fly ash filled PVC composites along milling direction (MD) ...............................................................................................104
Table 8.4: Mechanical properties of KB and KC filled PVC composites along milling direction (MD) .........................................................................................................................104
Table 8.5: Mechanical properties of untreated and treated fly ash filled PVC composites in transverse direction (TV) ............................................................................................106
Table 8.6: Mechanical properties of KB and KC filled PVC composites in transverse direction (TV) .........................................................................................................................106
CHAPTER 1

INTRODUCTION

1.1 Background

Globally, the most important application of the beneficiation of coal fly ash is in its partial replacement for Portland cement in the cement and concrete industry. The application of fly ash as an engineering material primarily originates from its pozzolanic nature, spherical shape, and relative uniformity.

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 reduced 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 reason is the 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 may be profitable. Very little work has been done in this field, and the surface properties of fly ash are little understood. Alkan et al [1995] studied the incorporation of fly ash into polyethylene and Ma et al [2001] 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 [Kruger, 1999] but its application remains limited.

In this study, the surface properties of untreated South African fly ash are investigated; and subsequently, the feasibility of altering its characteristics and surface reactivity are tested using
a surfactant. No other references could be found where the surface of South African coal fly ash was chemically modified. Furthermore, the feasibility of application of the untreated and surfactant treated fly ash as inorganic fillers in PVC are tested.

1.2 Fly ash

Fly ash (FA) is a residue that is generated from the combustion of coal in power stations. It contains small amounts of residual carbon that was not completely combusted, which gives the fly ash its characteristic grey colour, Figure 1.1. The composition of fly ash varies according to the source, method of combustion and the composition of the coal [Vassilev, 1996]. It can be classified into a variety of particle size fractions, some characterised by hollow silica-alumina glass spheres, called cenospheres [Potgieter-Vermaak, 2005].

![Sample of raw fly ash](image)

Figure 1.1: Sample of raw fly ash

Fly ash consists of an inorganic crystalline skeleton, covered with a glass phase of varying compositions [Kruger, 1997]. Its main constituents are silicon dioxide, (SiO$_2$), found in both amorphous and crystalline phases, aluminium oxide (Al$_2$O$_3$), iron oxide (Fe$_2$O$_3$) and calcium oxide (CaO). These phases are also the main building blocks of many coal bearing rock divisions.

Since fly ash is obtained from coal combustion, it is useful to have some insight into the chemistry and geology of the coal from which a specific ash was obtained. There are different types or ranks of coal namely: anthracite, bituminous, sub-bituminous, lignite and others. The
chemical content of the burned coal has great influence on the chemical properties of the produced fly ash [Schmidt, 2008].

Fly ash is generally classified into two classes namely Class F and Class C. The grouping depends on the kind of coal combusted to generate the fly ash and the amount of oxides present in the ash. Fly ash that contains less than 10 percent of CaO is classified as Class F while a Class C fly ash contains more than 10 percent of CaO [Vempati, 1994].

Class F fly ash is generated from the combustion of hard and older coals, i.e. anthracite or bituminous coal, and the obtained ash is pozzolanic in nature with at least 70% of the percentage weight of the ash consisting of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$. Class C fly ash is obtained from the combustion of younger coals, i.e. lignite or sub-bituminous coal, and is both pozzalonic and cementitious in nature with at least 50% of the percentage weight of the ash consisting of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ [Kruger, 1997 and Landman, 2003]. South African fly ash is classified as Class F.

The main source of power generation in South Africa is coal-fired power thermal stations which currently produce about 30 million tons of fly ash annually. Of the produced ash approximately 1.4 million tons (≈ 5%) are employed beneficially. The highest percentage of the used ash is for the production of cement extensions and concrete [Potgieter-Vermaak 2005].

The great amounts that are not used pose significant environmental and economical challenges and therefore there is a great need of environmentally safe and economically affordable ways of disposal and handling. There has been global interest to increase the utilisation of coal fly ash. Benefits for doing so include a reduction in the usage of non-renewable natural resources and the substitution of materials that may be energy intensive to manufacture.

1.2.1 Utilisation of fly ash

Recently, Ahmaruzzaman [2010] and Blisset [2012] published a review article on the utilisation of fly ash. In these papers they discussed current and potential applications of coal fly ash, including its utilisation in cement and concrete, as an adsorbent for the removal of organic compounds, waste water treatment, light weight aggregates, zeolite synthesis, mine
back fill and road construction. However, no reference is given to the application of fly ash as mineral filler in the polymer manufacturing industry. Some of these applications will be discussed briefly.

**a. Cement and concrete**

The low density and morphology of fly ash; in particular its sphericity, makes it an advantageous additive to cement and concrete [Copeland, 2011]. Fly ash has been reported to reduce the water requirement per amount of cement used. Improvement on the overall density of the concrete is observed when fly ash is introduced because of the decrease in voids and capillary pores in the cement, therefore increasing the flow and workability of the concrete [Caires, 2011; Siddique, 2001].

Fly ash also converts free lime found in cement or concrete into calcium silicate hydrate (CSH) which acts as a binder for the cement. CSH greatly contributes to the concrete paste’s strength and durability [Ramachandran, 2001]. The pozzolanic reaction of fly ash with free lime then increases fly ash’s cementious nature and therefore it can be deduced that fly ash increases the strength and durability of concrete [Siddique, 2001]. Studies have shown that even though the strength of the concrete prepared from fly ash might be lower than that of pure cement concrete before 28 days, it is equivalent at 28 days and after a period of a year or longer it is significantly higher [Obla, 2008].

The utilisation of fly ash in cement also increases its ability to withstand attacks from chlorides and sulphates. By reacting with free lime and reducing the quantity of free aluminates, fly ash prevents sulphates and chlorides from attacking the concrete and causing fractures [Tikalsky, 2003; Siddique, 2001].
b. Soil ameliorant

Fly ash can be used as an ameliorant for the improvement of the physical, chemical and biological properties of damaged soils such as mine soils [Kruger, 2009]. This improvement can lead to elevated soil efficiency due to increased nutrition retention and better leaching capabilities.

Nutrient and pH imbalances in problem soils can be corrected with the use of fly ash. The trace element content of fly ash in conjunction with the organic nature of the soil itself is believed to have beneficial effects on plant growth [Jala, 2004]. Fly ash has also been reported to improve the water retention capacity of soils [Iyer, 2001].

A combination mixture of fly ash with sewage sludge and lime (forming SLASH- Sludge, Lime and fly Ash) was used to develop an artificial soil. The SLASH soil was investigated on sandy, loam and acidic soil and the authors reported enhanced initial plant growth [Reynolds, 1999; and Truter, 2000].

c. Wastewater Treatment

The use of fly ash as an adsorbent of heavy metals in wastewaters was found to reduce its toxicity by the removal of toxic substances; phosphates, nitrates, copper (Cu) and lead (Pb) [Gupta and Torres, 1998]. Bada and Potgieter-Vermaak [2008] studied the properties of fly ash as an adsorbent for organic compounds in wastewater. They treated fly ash with a strong acid (HCl) which resulted in an increase in the specific surface area and resultant changes to the surface properties of the ash, leading to an improvement in the adsorption capacity of the ash.

Acid mine wastewaters contain heavy metals which are highly acidic and can be problematic if they leach into the ground or end up in the water main streams. Gitari et al [2008] reported on the use of fly ash for mine wastewater treatment as an alternative for limestone, lime and sodium hydroxide. At controlled pH levels, the concentration of heavy metals was reduced significantly, lowering the acidity of the wastewater.

The adsorption of lead onto NaOH treated fly ash was reported by Woolard et al [2000]. The treated fly ash samples have shown an increase in adsorption capacity compared to the
untreated ash. Madzivre et al [2009] studied the treatment of mine waste water with fly ash for the removal of sulphates instead of chemical or biological treatments. This was reported to be cost effective because fly ash itself is a waste product and can be accessed with ease from coal power stations for use in the treatment of mine waste waters.

d. Toxic waste Treatment

Reynolds et al [1999] reported on the use of fly ash in neutralising toxic sewage sludge. It was found that the sewage sludge can be recycled and applied to agriculture through treatment of the substance with fly ash. Eye and Basu [1970] studied the conditioning of sewage sludge with fly ash and found that it can be useful in the recycling of wastewater.

e. Mine Backfill

The use of fly ash as a backfill in mines has found much interest of lately. Knowing that fly ash can be used as a soil ameliorant, an adsorbent for organic compounds and toxic materials and that it is cementious, adds value to its suitability for use in backfilling [Ward, 2006]. Ward mentioned a number of advantages of using fly ash in mine back filling, including void filling, stabilisation of soil cover, improvement of water retention and many more.

f. Mullite and glass ceramics production

The high content of SiO$_2$ and Al$_2$O$_3$ in fly ash makes it a suitable material for the development of mullite and glass materials [Suriyanarayanan, 2009]. It is also considered to be an affordable resource for the glass and ceramics industry acting as a replacement for kaolinite [Blissett, 2012]. In their studies, Suriyanarayanan [2009] and Iyer [2001] both observed that an equal ratio (1:1) of coal ash and alumina was required to develop a homogenous mullite composite. Tan [2011] studied the development of mullite whiskers from coal ash and reported good diameters for the products. Glass and ceramics produced from coal fly ash have been reported to have comparable physical and mechanical properties to available literature values for these materials [Blissett, 2012].
g. Inorganic Filler into Polymers

Fillers are generally used in polymeric materials to reduce their production costs and to improve selected characteristics of the final product. The physical properties of fly ash, in particular its spherical shape, Figure 1.2, facilitate dispersion and fluidity making it suitable for application as filler. Furthermore, compared to conventional fillers, for example CaCO$_3$ or SiO$_2$, the low density and cost of fly ash adds to the list of its advantages.

![Figure 1.2: Spherical nature of fly ash particles observed under a scanning electron microscope](image)

Research in the field of utilizing fly ash as filler in different polymeric materials is growing exponentially. Examples of these studies includes the work by Alkan [1995] who studied the incorporation of fly ash into polyethylene; while Ma [2001] investigated changes in the properties of fly ash–polypropylene systems after coupling agents were added.

Yang et al [2006] studied the surface modification of purified coal fly ash, with subsequent application in polypropylene. One of the principle problems that occur when fly ash is used as filler in polymers is that there are no binding interactions between the polymer and fly ash, with the consequence that the quality of the product is unsatisfactory. If the surface properties of fly ash can be modified in such a way that this problem is conquered, a new market for the utilisation of fly ash can materialize.

Nath [2010a and 2010b] addressed this problem by studying the effect of surfactant modified fly ash on the properties of composite films fabricated with polyvinyl alcohol (PVA). Their results showed an enhancement in the physical properties of the polymer, which they attributed
to the elimination of particle-particle interaction, and a better distribution of fly ash within the polymer.

1.3 Surfactants

Surfactants are surface active agents. They are amphiphilic substances consisting of a lyophilic (or hydrophilic) part which is a polar-group, and a lyophobic (or hydrophobic) part which is generally a hydrocarbon chain [Tadros, 2005]. Due to their amphiphilic nature, surfactants tend to concentrate at interfaces and assemble into aggregates, such as micelles and vesicles, in bulk solution.

Surfactants can be classified into non-ionics and ionics, where the ionics can be further divided into three groups namely; cationics, anionics, and zwitterionic, as shown in Figure 1.3.

![Figure 1.3: Surfactant classification according to the charge of their head group](image)
Non-ionic surfactants can be defined as surfactants that have no charge in the predominant working pH range. These surfactants dissociate into two neutral parts resulting in a final charge of zero [Porter, 1994]. The non-polar part of the nonionic surfactants is mainly characterised by a polyether or polyhydroxyl unit with an oxyethylene unit as a polar part [Malik, 2011].

Ionic surfactants are amphiphilic substances that have an ionic group that is attached directly or through intermediates to a hydrocarbon chain. The ionic group of the surfactant acts as the surface active entity [Malik, 2011].

Surfactants can be used to alter the physical properties of certain materials. Treatment of a charged surface with an ionic surfactant can change its hydrophobic or hydrophilic nature. For example, for a negatively charged material; treatment with a cationic surfactant may cause it to become hydrophobic while an anionic surfactant may render the material hydrophilic and vice versa [Rosen, 2012].

The interaction of a nonionic surfactant with a surface depends on the physical properties of the material, and may lead to formation of a hydrophobic or hydrophilic surface. For a polar surface, for example, the hydrophilic part of the surfactant will interact with the surface and render it more hydrophobic [Malik, 2011 and Rosen, 2012].

Zwitterionic surfactants, however, tend not to significantly alter the surface charge of materials or their physical properties. Having both positive and negative charges, they can interact with a surface material with both head groups resulting in a neutralized effect [Rosen, 2012].

1.3.1 Cationic surfactants

Cationic surfactants are classified as such if their molecules dissociate in solution to form a surface active cationic entity and a normal anion [Tadros, 2005]. Cationic surfactants are subdivided into four main classes according to their chemical structure; alkyl amines, ethoxylated amines, alkyl imidozolines and quaternaries.

Figure 1.4 gives an example of a cationic surfactant with an alkyl amine chemical structure. Their applications include hydrophobisation, where the surfactants act as corrosion inhibitors,
anti-caking agents in fertilisers, floating agents, adhesion promoters, and as dispersants for mineral fillers.

Figure 1.4: Example of a Cationic Surfactant, Trimethylhexadecyl Ammonium Chloride

1.3.2 Anionic surfactants

Anionic surfactants (detergents) are amphiphilic substances that have an anionic group attached to a long hydrocarbon chain. The anion is the surface active entity and the length of the carbon chain increases their detergency strength. Surfactants with a hydrocarbon chain of 12-16 carbon atoms have been reported to be strong detergents [Tadros, 2005]. The counterions of anionic surfactants are mainly sodium, potassium, ammonium, magnesium and calcium. Sodium and potassium are used because they give the surfactant increased water solubility while magnesium and calcium are suitable for oil solubility. Amine counterions cause the surfactant to be both water and oil soluble [Malik, 2011].

There are three important anionic groups that are mainly used, namely: the sulphates (-$\text{OSO}_3^-$), sulphonate (-$\text{SO}_3^-$) and carboxylates (-$\text{CO}_2^-$) [Lange, 1999]. An example of sulphonate anionic surfactant is shown in Figure 1.5. Anionic surfactants are characterised by high dispersing and foaming properties.

Figure 1.5: Example of an Anionic Surfactant, Sodium dodecylbenzenesulphonate
They are highly stable but are sensitive to hard water (i.e. the presence of metal ions) and changes in pH. Anionic surfactants are relatively basic and tend to protonate under conditions of low pH values and precipitate in the presence of metal ions [Tadros, 2005]. An advantage of using anionic surfactants is that they are affordable and easily accessible.

### 1.3.3 Critical Micelle Concentration (c.m.c)

Micelles can be defined as small colloid particles composed of molecules of a surface active substance. The formation of these micelles on a solid surface by surfactants is driven by the amphiphilic nature of the surfactants [Dominguez, 1997].

For surfactants, there exists a concentration above which the surfactant begins to form aggregates (micelles) spontaneously and any increase in the concentration leads to the formation of micelles [Lange, 1999]. This effect is shown in Figure 1.6. The concentration at which micelles are formed is known as the critical micelle concentration (c.m.c). The c.m.c can also be defined as a measure of surfactant efficiency; the lower the c.m.c the less surfactant is required to saturate the system and induce the formation of micelles. [Rosen, 2012]

![Figure 1.6: Representation of a spherical micelle [Dominguez, 1997]](image)

The surface of a solid material exposed to a surfactant solution changes rapidly with an increase in the concentration of the surfactant. This occurs before the c.m.c. is reached and surface tension remains fairly constant above the c.m.c. [Floriano, 1998].
Micellisation is dependent on temperature conditions, the length of the surfactant alkyl chain as well as the concentration of the surfactant. Temperature effects are mostly prominent for ionics and zwitterionics and the c.m.c decreases with increasing temperature. The hydrophobic part of the surfactants tends to change with varying temperature conditions [Kim and Lim, 2003]. The length of the alkyl chain influences both the c.m.c and the hydrophobicity of surfactants. An increase in chain length will increase both the c.m.c and the hydrophobicity [Atkin, 2003b].

1.3.4  Mechanism of surface surfactant adsorption

Surfactant surface adsorption at different interfaces; liquid-liquid or solid-liquid, has been reported to be essential in many industrial process applications, including metallic surface interactions, detergency and many more [Schniepp, 2007; Sammalkorpi, 2008]. Understanding surfactant adsorption on solid surfaces in an aqueous surfactant solution has received increased attention in recent years as seen by the number of different studies on different substrates that include fly ash, graphite, silica, fiber, gold and many more [Goloub, 1996; Sammalkorpi, 2008].

The aggregation of both ionic and non-ionic surfactants has been investigated either on hydrophilic (silica) [Goulob, 1996; Moglianetti, 2009] or hydrophobic (graphite) [Sammalkorpi, 2008] substrates. Many reported that surfactant adsorption is dependent on the nature of the substrate as well as the concentration of the surfactant.

Electrostatic attractions (van der Waals interactions) are considered to be the main driving force for interactions between ionic surfactants and oppositely charged hydrophilic surfaces. The interaction of hydrophobic substrates with ionic surfactants is reported to be primarily due to the hydrophobic interaction between the surfactant’s tail and the substrate [Manne, 1994; Atkin, 2003a].

The aspects of surfactant adsorption have been accepted to some extent but there is some room for further development of the existing theories. The interaction of surfactants and surfaces can be explained by two different models; the three or four region model and the two-step model [Atkin, 2003a; Manne, 1994]. Each region in these models indicates the progression of
surfactant aggregation and surface coating/coverage. The two-step model is mainly associated with aqueous ionic surfactants [Manne, 1994].

The four region model is shown in Figure 1.7. The x-axis, C, of the isotherm represents the residual surfactant concentration while the y-axis, Γ, denotes the adsorption density of the surfactant onto a surface. The four region model can then be explained as follows: region I represents electrostatic adsorption of surfactant monomers with head groups interacting with the substrate, region II is the beginning of surface coverage due to interaction between adsorbed surfactant monomers, hemimicelle formation, the hydrocarbon tail forms hydrophobic areas on the surface, region III represents the growth of the hemimicelles formed in region II with the same total coverage and the hydrophilic parts are formed with the head-groups in solutions, and region IV is where the c.m.c is reached and full micelles are formed spontaneously [Atkin, 2003a]. Atkin et al [2003a] defined hemicelles as “a spherical structure with surfactant head-groups facing both towards the substrate and into the solution”

Figure 1.7: The four region model of surfactant adsorption as from Atkin 2003 (a)

The two-step model consists of two plateau regions, as represented in Figure 1.8. The pre-hmc (hemimicelle concentration) plateau occurs at low surfactant concentrations and the saturation level plateau occurring above the c.m.c. with a high increase of surface coverage observed above the c.m.c. The pre-hmc plateau is characterised with two parts, the electrostatic adsorption of surfactant on the substrate and the neutralization of the surface charge with increased surfactant monomer adsorption approaching the hmc.
The saturation plateau level also consist of two sections, the occurrence of hydrophobic interactions between adsorbed monomers leading to the formation of hemicelles and the formation of micelles with high surface coverage [Atkin, 2003a].

![Diagram of surfactant adsorption](image)

**Figure 1.8:** The two-step model of surfactant adsorption as taken from Atkin 2003 (a)
The regions presented in the figure are (I) a low surface excess region, (II) the first plateau region, (III) a hydrophobic interaction region and (IV) the second plateau.

### 1.3.5 Counter ion effect on surfactant aggregation

Columbic forces have been attributed as the primary forces that influence the formation of ionic surfactant-surface aggregates [Bitting and Harwell, 1987]. Electrolytes have been found to have a great influence on the aggregation patterns of ionic surfactants in relation with the counter ion and ionic micelle interaction that can occur during micellisation [Umlong and Ismail; 2006].
Bitting and Harwell [1987] reported on the importance of counter ions in surfactant-surface adsorption. They found that adding NaCl to the surfactant solution increased the adsorption plateau, on an alumina surface, with increasing concentration of the salt. Wanless et al [1997] also observed the same trend on a graphite surface and concluded that aggregation can form on the surface at concentrations below the c.m.c in the presence of NaCl and other counter ionic salts. Silbert et al [2010] reported that the hydrophobicity and hydrophobic interactions of surfactant aggregates formed on substrates can be affected by the counterions of the surfactant.

Atkin et al [2003b] observed an increase in the rate of adsorption of different surfactants, investigated in his study, in the presence of electrolytes added to the surfactant aqueous solution in the form of salts.

Counter ions and additional electrolytes in ionic surfactant solutions tend to decrease the c.m.c of the surfactant and therefore influence the formation of surfactant aggregates on a surface interface. Counter ions also decrease the repulsive forces that may exist between the ionic head groups of the surfactant and a surface and therefore allowing for better interaction and therefore increased chances of micellisation [Ulong and Ismail; 2006; and Paria, 2004].

**1.4 Study Objective**

The purpose of this study is to report on the characterization of the surface of a typical South African coal fly ash, modified by Sodium Lauryl Sulphate (SLS), and to elaborate on the problems and challenges experienced in characterization of the product.

The effect of water on the untreated fly ash sample was also investigated by comparing the results under similar conditions to samples exposed to different concentrations of the surfactant solution. Untreated and SLS modified fly ash samples were used as filler for polyvinyl chloride (PVC) and their mechanical properties were investigated in comparison to two different calcium carbonate fillers.
1.5 Reference


52. Ward CR, French D, Jankowski J, Riley K, and Li Z, 2006, Use of coal ash in mine backfill and related applications, CCSD.
CHAPTER 2
THEORETICAL DESCRIPTION OF ANALYTICAL TECHNIQUES

2.1 X-ray Powder Diffraction (XRD)

X-ray powder diffraction is a non-destructive analytical technique used for the characterisation of crystallographic structure, grain size, and preferred orientation in powdered solid samples. It can also be used to determine relative abundance of crystalline substances in solid materials.

XRD is based on two phenomena: (a) the scattering of X-rays by the electron cloud of each individual atom, and (b) the interference of the scattered X-rays [Guiner, 1963]. In 1912, M. von Laue discovered the nature of interaction between X-rays and crystalline substances. He suggested that the scattered X-rays can interfere with one another constructively, resulting in the wavelength of the diffracted X-rays being similar to the interatomic spacing of a crystal lattice [Moore, 1997].

The interference pattern of the scattered X-rays is explained by Bragg’s law \( n\lambda = 2d \sin \theta \). If the wavelength, \( \lambda \), of the diffracted X-rays and the angle, \( \theta \), at which they were produced, the interatomic distance, \( d \), of a crystal can be determined, with \( n \) being an integer [Moore, 1997].

During measurements of an XRD pattern, a sample is radiated with a monochromatic X-ray beam from a cathode tube. The incident rays interact with the sample to produce diffracted rays according to Bragg’s law, as shown in Figure 2.1. The intensity of the diffracted X-rays is detected, with all the possible diffraction patterns of the sample attained. The diffraction peaks lead to the identification of crystalline phases using the interatomic spacing of the crystalline phase. Each phase in a heterogeneous sample has a unique interatomic space and thus the characterisation of an unknown sample is possible [Dinnebier, 2008].
The XRD technique is quick in identifying unknown inorganic materials; it provides unambiguous mineral identification, while sample preparation and data interpretation is fairly easy.

2.2 X-ray Fluorescence (XRF)

XRF is an analysis technique used for elemental analysis of solids with detection limits that are in the range of 1 ppm [Wirth, 2011]. It is a non-destructive analysis method, requiring a significant amount (approximately 1 g) of a finely ground analyte. Sample preparation for XRF analysis is relatively easy and cost effective.

XRF is dependent on the absorption of radiated X-rays. The absorbed X-rays excite the sample’s atoms leading to ionisation (Figure 2.2) where an inner electron (lower energy orbital) of the atom in a sample is displaced, making the atom unstable [Birkholz, 2006]. An outer electron (higher energy level) then replaces the missing inner electron and energy is released. The released energy represents the energy difference of the binding energies of the higher and lower energy levels [Jenkins, 1999].

Characteristic X-rays are emitted during the energy release, representing the atoms present in the sample. The emitted X-rays depend on the chemistry of each atom present in the sample and are emitted at different wavelengths corresponding to a certain atom. The wavelengths at which X-rays are emitted are plotted on a spectrum and give information about the identity of the elements in the sample [Williams, 1987].

Figure 2.1: Diffraction of X-rays by a crystalline substance
The concentration of a species in an analyte is determined by measuring the intensity of the emitted X-ray. The relationship between the concentration of elements in a sample and the characteristics X-ray intensities was first established in the mid-1950s, and has become the basis of the “fundamental parameters” approach of the calibration of XRF [Thomsen, 2007].

XRF is said to be a qualitative and quantitative analysis technique because it can identify elements as well as quantify them. Its applications extend over a variety of disciplines including chemistry, geology, environmental sciences, industry and many more.

### 2.3 Raman and Infrared spectroscopy

Raman and infrared spectroscopy are the main analytical techniques used to study the vibrations of atoms in molecules. The energy of vibrations are measured with infrared spectroscopy after absorption of infrared light from a polychromatic source, while Raman spectroscopy measures the energy of scattered light after irradiation with a strong monochromatic light (laser) [Larkin, 2011].
Raman and infrared spectra can be described as a fingerprint of a material and can therefore be used for identification purposes. The chemical and physical structure of materials can be studied with the two techniques [Smith, 2005]. Infrared spectroscopy can also be used for quantitative analysis, while Raman spectroscopy can also be used for semi-quantitative analysis.

Both techniques can be applied to a wide range of samples, including gases, liquids and solids, with little or no sample preparation. Although useful in a wide range of applications, Raman spectroscopy sometimes has a problem with sample degradation under the strong laser light and fluorescence might interfere with recording of the Raman spectrum. Thus Raman spectroscopy is less widely used in comparison to infrared spectroscopy [Smith, 2005].

2.3.1 Infrared (IR) Spectroscopy

IR spectroscopy was first commercialised during the 1940’s. Prisms were used as dispersive elements until the mid-1950s when diffraction gratings were implemented [Stuart, 2004]. A great improvement to IR spectroscopy was the understanding of Fourier-transformation mathematics, which improved the quality of IR spectra and minimised the time required to acquire data – from there the term FTIR (Fourier-transform infrared spectroscopy) was introduced [Christy, 2001].

A sample irradiated with infrared electromagnetic energy will either absorb or transmit the energy. For a vibration of a molecule to be active in infrared spectroscopy, its electric dipole moment must change during vibration. Vibrations are broadly classified according to the type of movement, namely stretching and bending [Stuart, 2004]. These are explained in Figure 2.3.

Each molecule is characterised by a certain number of vibrational degrees of freedom according to the number of atoms forming the molecule. For a linear molecule there are 3N-5 degrees of freedom while a non-linear molecule has 3N-6 degrees of freedom (N = number of atoms in a molecule). Vibrational modes, both stretching and bending, occur at different frequencies according to the type of bonds that exist in a molecule and the masses of the individual atoms involved in a vibrational mode [Smith, 1996].
2.3.2 Raman Spectroscopy

The Raman effect was first discovered in 1928 by C.V. Raman, who won a Nobel Prize in Physics in 1930 for this breakthrough. He conducted his studies on liquid samples and a few years later G. Landsberg conducted the same study on crystal structures [Larkin, 2011].

Compared to IR spectroscopy, Raman spectroscopy was not widely used in laboratories as the effect was very small and difficult to measure. Only with the availability of lasers as strong monochromatic sources and the use of computers to enhance the signal electronically, did Raman spectroscopy become a technique that is today available in most analytical laboratories [Smith, 2005].

In a Raman experiment a sample is irradiated with strong monochromatic light (laser), which excites the molecules to a higher virtual energy state. Once the molecules return to a normal energy level, light is scattered into all directions and three possibilities exist. These are illustrated in Figure 2.4. Firstly, most of the light is elastically scattered (Rayleigh scattering) where the energy of the incident light is equal to that of the scattered light, Figure 2.4a [Wartewig, 2003].
Secondly, molecules in the ground vibrational state fall back to a higher energy level in which case the scattered light is at a lower energy level than the incident light, namely Stokes Raman spectroscopy, Figure 2.4b. And thirdly, in Anti-Stokes Raman shown in Figure 2.4c, molecules that are at a higher energy level fall back to the ground state after excitation and the energy of the incident light is lower than that of the scattered light [Wartewig, 2003].

As most molecules are in their ground state at room temperature, the Stokes scattering is much stronger than the Anti-Stokes and are most commonly used [Wartewig, 2003]. In some instances the strong laser light might also excite an electron to the next energy level, which is the cause of fluorescence which can interfere with a Raman spectrum (see Figure 2.4).

2.4 Thermogravimetric analysis (TGA-FTIR)

Thermogravimetric analysis (TGA) is one of many primary thermal analysis techniques. Thermal analysis is defined as “the analysis of a change in a property of a sample, which is related to an imposed temperature” [Brown, 2001]. TGA measures the change in the weight of a sample as a function of temperature or time in a controlled environment. It can be conducted in three different ways namely; under dynamic measurement that is at a constant heating rate, isothermal measurement that is constant temperature, and controlled TGA which involves non-linear temperature programs [Gabbott, 2008].
TGA is mainly used for the determination of the purity, composition and thermal stability of sample materials. It uses the properties of the analysed material for characterisation, by measuring the change in weight due to volatility, oxidation, dehydration or decomposition [Haines, 2002]. The obtained thermogravimetric curves (weight versus temperature or time) are characteristic to the material being analysed. The curves give an indication of weight loss or gain due to a certain process at a particular temperature or time [Gabbott, 2008].

The integration of TGA with other instruments has been found to be greatly helpful in determining the composition of the analysed material. TGA-FTIR (integration of TGA with FTIR spectroscopy) allows for the identification of evolved gases from the analysed material during a TGA analysis [Brown, 2001]. The obtained IR spectra can be used together with the TGA curve for complete analysis of the material by comparing the process that occurred during temperature changes and the chemical composition of the evolved gas.

TGA-FTIR can be used for the analysis of materials such as polymers, plastics, composites, organic and inorganic substances. However its application is limited to substances that are subjected to mass loss and gas formation [Brown, 2001].

### 2.5 Scanning Electron Microscopy (SEM)

In 1938 M. Von Ardenne worked and published the principles of the scanning electron microscopy. The first instrument was built by Sir C. Oatley and it was commercialised in 1965 [Voutou, 2008].

The SEM is primarily designed for imaging rather than chemical analysis. SEM images are produced by the scanning of a sample with a high-energy beam of electrons in a raster scan pattern to cover the whole sample site [Egerton, 2005]. The interaction of the sample’s atoms with the electrons results in the production of signals that have information concerning the sample’s surface topography (texture), morphology (shape and size of particles) chemical composition, and crystallographic information (atom arrangement); depending on the type of image signals used [Reed, 1996].

Secondary electron (SE) images, which show topographic features, together with the backscattered electrons (BSE) images, which give the compositional variations in a sample, are the most commonly used image signals [Reed, 1996]. The output of the SEM can therefore be
specified to be either topographic or compositional (compositional referring to the mean atomic number of the sample). SEM cannot distinguish between individual elements.

The main components of a SEM instrument are as follows: the electron source, focussing lenses (electromagnetic), sample chamber, detector, and display system. The most commonly used electron source is an electron triode gun fitted with a hot tungsten filament of about 0.1 mm in diameter. The electron gun is heated by a current of approximately 2.5 A to a point where “thermionic” emission takes place; thus giving the electrons enough thermal energy to overcome the potential barrier at the surface [Reed, 1996].

The electron gun and the electromagnetic lenses (focussing lenses) are housed inside the electron column. The gun emits electrons and accelerates them to energy levels in the range of 0.1–30 keV; the lenses influence the travelling path of the electrons while focussing them into a fine beam. The electron beam then leaves the electron column through the final lens into the sample chamber, where sample-electron beam interaction occurs. The interaction occurs at a depth of field of about 1 μm, generating signals that then form an image of the analysed sample.

The generated signals are collected from the beam-sample interaction. These interactions differ from one point on the sample to another. The collected signals are then converted to point by point intensity changes to produce an image using SE and BSE image signals according to the type of analysis. The generated images are digitalised and displayed for analysis.

SEM is advantageous over other electron microscopes because it can focus on large areas of analysis sites of a sample at a time due to its large depth of field [Standländer, 2007]. It has high image resolution with strong feature specificity. Sample preparation is fairly easy.

A number of limitations have been reported concerning scanning electron microscopy. The most important are that the nature of sample analysis, which occurs in vacuum, presents problems for powder material analysis, and the generated images do not show the true colour of the analysed material.
2.6 Transition Electron Microscopy (TEM)

Transmission Electron Microscopy was the first kind of Electron Microscopy to be developed. The first TEM image was obtained by Ernst Ruska and Max Knoll in Germany in 1931 [Voutou, 2008].

TEM is a microscopy analysis technique that uses a beam of electrons transmitted through a thin sample, approximately 5 nm to 0.5 μm in thickness. It uses an electromagnetic lens system to focus the thin electron beam onto the sample. The electron energy of the electron beams ranges between 60 and 150 keV [Egerton, 2005].

TEM can use three different electron beam-specimen interactions for sample analysis, namely; unscattered electrons from the transmitted beam, the elastically scattered electron from the diffracted beam and the inelastically scattered electrons. [Voutou, 2008]

Transmitted unscattered electrons are responsible for the visibility of the images obtained during analysis. There exist an inversely proportional relation between the transmission of unscattered electrons and sample thickness, thus the primary requirement for thin samples for analysis. Thick samples cause the images to be dark due to diminished transmitted unscattered electrons.

Sample orientation and atomic arrangement are achieved from scattered electrons obtained from the interaction of electrons and the atoms present in the sample. The use of inelastic interaction between the electrons and atoms in the analysed sample allows for instrument integration for further analysis, for example the Electron Energy Loss Spectroscopy.

For optimum results certain conditions are required for TEM, which are sometimes also considered as limitations to the instrument. Due to the high vacuum requirements during analysis, the thin sample specimen needs to be absolutely dry, without any traces of water. Sample stability is also important, especially when exposed to the electron beams [Bouchet and Gaillard, 2005].
2.7 Particle Size distribution

Particle Size Distribution (PSD) analysis is used to measure the size and range of particles in a particular substance [Stanley-Wood, 1992]. Particles are 3-dimensional objects with three parameters (length, breadth and height) which are necessary for their full description [McDonagh, 2010]. Many particle sizing techniques assume that the material being measured is spherical. The advantage of this assumption originates from the single parameter (diameter) which is a description of the sphere. The assumption simplifies particle size distribution presentation but it can produce inconsistent results when non-spherical particles are analysed [Cooper, 1998].

Laser diffraction has become a favoured analysis method for determining particle size distribution of aerosols, suspensions emulsion and solid samples. It is a robust particle measurement technique that can be used for both dry and wet samples. The size analysis range of laser diffraction lies between 0.02 to 2000 microns [McDonagh, 2010].

Laser diffraction based particle size analysis is based on the scattered light generated when a laser beam is applied onto particles. The interaction of laser light with the particles produces diffraction of the laser light. The Fraunhofer and Mie theory are mathematical theories that can be used to describe the interaction between the laser light and the particles. The theories state that for a single spherical particle, the diffraction pattern shows a typical ring structure [Cooper, 1998]. The Mie theory has been adopted for application in laser diffraction.

Light scattering occurs at an angle that is directly proportional to the size of the interacting particle. The scattering angle increases logarithmically with decreasing particle size. Scattering is dependent on the particle sizes; large particles scatter light at narrow angles with high intensity whereas small particles scatter at wider angles with low intensities [Allen 1997].
2.8 References


CHAPTER 3

EXPERIMENTAL

3.1 Materials

The analysed coal fly ash in this study is SuperPozz® ash with 95% of its particles having a diameter of less than 5 μm. It was obtained from the Ash Resources (Pty) Ltd Ash beneficiation site at the Lethabo Thermal Power station located in the Free State, South Africa.

Sodium Lauryl Sulphate (SLS) with a purity of 98% was obtained from Merck, and was used with no further purification.

3.2 Coal Fly Ash modification

A quantity of 10 or 20 g of the dry fly ash sample was weighed and treated with the surfactant solution, sodium lauryl sulphate (SLS), in a 1:10 solid:liquid ratio. Different concentrations of the surfactant solution (0.1%, 0.5%, and 2.0% by weight) were studied at different temperature conditions (30, 50, and 80 °C) as well as exposure times (6, 18, and 66 hours). The effect of water on the properties of the fly ash sample was investigated by comparing the results to samples where only distilled water was used under similar treatment conditions.

The fly ash-surfactant mixtures were placed in a WiseBath® WSB digital precise shaking water bath, obtained from Daihan Scientific, which was controlled at the relevant temperature with continuous shaking at 130 revolutions per minute.

For the reflux experiments, a reflux system consisting of a heating mantle, round bottom flask and condenser was assembled. The mixtures were refluxed for 6 hours using water and SLS solutions with concentrations of 0.5%, 2.0%, and 4.0% by weight.

After the respective treatments, the samples were washed with distilled water numerous times under vacuum filtration. They were then dried in a laboratory oven at 50 °C for 2 days.
It is important to note that a fresh surfactant solution was prepared every day an experiment was conducted, this was done in order to minimise chances of decomposition of SLS that may occur during storage. Sugàr et al [1999] investigated the stability of SLS according to temperature, concentration, time, and material used for storage. They reported that the concentration of SLS can be influenced by time of storage especially if it is at low quantities. Bacterial growth was also observed for low concentrated SLS solutions, which could lead to contaminations.

3.3 Characterisation techniques

3.3.1 X-ray Diffraction (XRD)

X-ray powder diffraction analyses were performed on a PANalyticalX’Pert Pro powder diffractometer, Figure 3.1, with an X'Celerator detector and variable divergence- and receiving slits with Fe filtered Cu-Kα radiation. The phases were identified using X’PertHighscore plus software. The relative phase amounts were estimated using the Rietveld method (Autoquan Program). 20% of Si (Aldrich 99% pure) was added to the sample for the determination of the amorphous content. Each sample was milled in a McCrone micronizing mill and prepared for XRD analysis using a back loading preparation method.

Figure 3. 1: PANalyticalX’Pert Pro powder diffractometer
3.3.2 X-ray Fluorescence (XRF)

X-ray fluorescence analyses were carried out on an ARL9400XP + spectrometer (Thermo Fischer Scientific, Switzerland), Figure 3.2. The samples were ground to <75μm in a tungsten carbide milling vessel and roasted at 1000 °C to determine the loss on ignition. A mixture of 1 g of the sample and 6 g of Li₂B₄O₇ was then fused into a glass slide. Major element analyses were executed on the fused bead.

3.3.3 FTIR spectroscopy

Mid-infrared spectra were recorded with a Bruker 70v Fourier transform infrared (FTIR) spectrometer, Figure 3.3, by placing the finely grounded samples in a diamond ATR (attenuated total reflection) cell. The sample compartment was evacuated during the acquisitions and eliminated any contributions from CO₂ and water vapour in the atmosphere. The resolution was 2 cm⁻¹ and 64 scans were signal-averaged in each interferogram. Reflectance spectra were recorded with the Hyperion microscope attached to the same instrument. The spectra recorded with the ATR attachment are transmission spectra and represent the composition of the whole sample, while the reflectance spectra highlight the composition of the surface of the sample. Both techniques measured the bulk sample, that is the powder as whole and not individual particles.
3.3.4 Raman spectroscopy

Micro-Raman spectroscopy was performed with a T64000 micro-Raman spectrometer from HORIBA Scientific, JobinYvon Technology (Villeneuve d’Ascq, France). The Raman spectra were excited with the 514.5 nm line of an Innova 70v argon ion laser from Coherent and either the 50x or 100x objective of an Olympus microscope was used to focus the laser beam (spot size ~10 µm) on individual spheres (Figure 3.4) of the fly ash samples, and also collected the backscattered Raman signal.

An integrated triple spectrometer was used in the double subtractive mode to reject Rayleigh scattering and dispersed the light onto a liquid nitrogen cooled Symphony CCD detector. The laser power at the sample varied between 6 - 10 mW and most of the spectra were recorded with a 150 s acquisition time and 2 accumulations, but in some cases the accumulations were increased to result in smoother spectra.

Figure 3. 3: The Bruker 70v Fourier Transform Infrared (FTIR) spectrometer with microscope attachment (left) and the TX6400 Raman spectrometer (right).

Figure 3. 4: View of fly ash particles under the Raman microscope with 50x (left) magnification and 100x magnification (right)
Raman 2D mapping images were recorded with a WiTec Alpha 300AR instrument equipped with: an UHTS spectrometer, an EM-CCD camera operated in conventional mode, a 488 nm excitation laser and a Nikon glass corrected at 60x (NA = 0.8) air objective.

### 3.3.5 Thermogravimetric analysis (TGA-FTIR)

Thermal stability and evolved gas analyses were performed on a Perkin Elmer TGA 4000 Thermogravimetric Analyzer coupled to a Perkin Elmer Spectrum 100 FTIR spectrometer, Figure 3.5. Approximately 20 mg of the solid sample was placed in an alumina pan and heated in air at 10 ºC/min from room temperature up to 400 ºC

![Perkin Elmer TGA 4000 FTIR](image)

**Figure 3.5: Perkin Elmer TGA 4000 FTIR**

### 3.3.6 Scanning Electron Microscopy (SEM)

Ash samples were mounted on a double sided carbon tape by dipping carbon stubs into the samples. Excess sample was removed from the carbon stubs by gentle blowing with compressed nitrogen. The samples were then coated with gold using a Sputter-coater (Emitech K550X, Ashford, England). The samples were viewed on a JEOL JSM 840 Scanning Electron Microscope (SEM), Figure 3.6, operated at 5 kV. Images were collected with the aid of a flame-grabber (Orion-version 6)
3.3.7 Transmission Electron Microscopy (TEM)

A JEOL JEM 2100F TEM, Figure 3.7, operated at 200 kV, was used to examine the structure and composition of the fly ash samples at high resolution. The fly ash sample studied was dispersed in 100% ethanol with the aid of sonication; after which a drop of the diluted suspension was poured onto a copper grid. The sample was left to dry before it was injected into the sample holder for analysis.
3.3.8 Particle size

Particle size distribution (PSD) of untreated and SLS-treated fly ash particles was obtained by laser diffraction using a Malvern Mastersizer 2000 fitted with a Hydro 2000G dispersion unit (Figure 3.8) obtained from Malvern Instruments Ltd. Worcester, UK. This was done in order to examine the effect of SLS treatment on the size distribution.

Scattered light data were recorded from 2000 to 5000 snapshots of 10 μs each. A polydisperse mode of analysis and a refractive index of 1.533 with an adsorption of 0.1 were chosen. Size data collection was performed at constant obscuration in the range 10 – 20%. Samples were run in duplicate with three runs per duplicate.

![Figure 3.8: Malvern Mastersizer 2000](image)

3.3.9 Contact angle

Contact angle measurements were used to obtain rapid information about the change in surface properties of the fly ash samples. These measurements were performed on an OCA-20 Contact Angle-meter (Data Physics Instruments), using the sessile drop method with water as wetting liquid. To perform these measurements, a small drop of water is deposited on the surface of a fly ash powder bed which was fixed to a microscope slide by double-sided tape. A picture of the profile of the drop is taken about 1 second after contact with the powder surface.
3.4 References

CHAPTER 4
CHARACTERISATION OF UNTREATED FLY ASH

4.1 Introduction

Fly ash is a complex and heterogeneous substance. Several characterisation techniques have been used and reported in literature to characterise its surface, chemical and physical properties. Guedes et al [2008] and Potgieter-Vermaak et al [2005] employed micro Raman spectroscopic analysis for the identification and characterisation of the different inorganic and organic substances that are present in fly ash.

Sarbak et al [2004] studied the surface properties of various fly ashes using numerous techniques including IR spectroscopy, XRD, thermal analysis and scanning electron microscopy. TGA-FTIR studies of fly ash were reported by Fermo et al [2000]. The decomposition of fly ash was observed according to temperature and time. Mahlaba et al [2011] reported on the particle size distribution of two different South African fly ash samples.

Similar techniques were used to characterise the Lethabo fly ash used in this study. XRD analysis was conducted to determine its mineralogical composition and phase identification. Elemental compositions were determined by the use of XRF analysis. Morphological and topographic characterisation was done with the aid of a SEM and TEM respectively. TGA-FTIR analysis was used to study the thermal stability while FTIR and Raman spectroscopy was used to identify crystalline phases as well as organic and amorphous material.

4.2 Qualitative and quantitative analysis of the chemical composition of Lethabo coal fly ash using XRD and XRF

Table 4.1 and Figure 4.1 give a presentation of the qualitative and quantitative results obtained from XRD analysis. The XRD spectrum shows the quantity of crystalline and amorphous materials present in the sample. Silicon was added to the sample as an internal standard.
Figure 4.1: XRD spectrum of untreated fly ash

Position [°2Theta] (Cobalt (Co))

Counts

Lethabo_FA-exp + Si

Peak List

01-079-1458; Mullite, syn; Al4.56 Si1.44 O9.72
00-027-1402; Silicon, syn; Si
01-078-1252; Quartz low, syn; Si O2
The Lethabo coal fly ash sample consists of an amorphous phase (glass) making up 62.1% of the total sample weight, with mullite ($3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2$) [Schneider, 2005] and quartz ($\text{SiO}_2$) as the main crystalline phases.

### Table 4.1: Quantitative XRD results of untreated Lethabo fly ash

<table>
<thead>
<tr>
<th>Phase</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>62.1</td>
</tr>
<tr>
<td>Mullite</td>
<td>31.8</td>
</tr>
<tr>
<td>Quartz</td>
<td>6.2</td>
</tr>
</tbody>
</table>

The quantitative XRD analysis of the untreated fly ash (Table 4.1) shows that 62% of the fly ash consists of an amorphous phase which in this instance is an alumina silica glass, consisting of a silicon-oxygen framework in which each silicon atom is surrounded by four oxygen atoms forming a tetrahedron (Figure 4.2) [Atkin, 2003a].

Cations such as $\text{Ca}^{2+}$, $\text{Na}^+$ or $\text{K}^+$ inserted into the polymeric structure breaks some of the connecting bonds, thus lowering the melting temperature of the glass. This results in silicon atoms that are connected to either 4, 3, 2, 1 or even no oxygen atoms [Tournie, 2008]. The $\text{Al}^{3+}$ atoms can be four-fold or six-fold coordinated. Due to this factor $\text{Al}^{3+}$ can be either a network forming or network-modifying cation in aluminosilicate melts.

![Figure 4.2: The silica-oxygen framework of a glass](image.png)
The elemental analysis of Lethabo coal fly ash obtained from the XRF analysis is summarised in Table 4.2. The sample was found to contain a very low percentage of moisture, carbonates and hydroxides, thus the low loss on ignition value. The percentage composition of CaO in the ash sample was found to be approximately 6%, confirming its Class F classification.

The elemental analysis is consistent with the different phases obtained from the XRD data and the low amount of fluxing ions (Na$^+$, K$^+$, Ca$^{2+}$, etc.) present indicates that the glass (amorphous phase) consists of a high percentage of silica.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>49.3</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>2.01</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>34.0</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>5.78</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
</tr>
<tr>
<td>MgO</td>
<td>0.99</td>
</tr>
<tr>
<td>CaO</td>
<td>5.06</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.87</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.24</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.59</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>0.07</td>
</tr>
<tr>
<td>NiO</td>
<td>0.05</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>0.04</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.08</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>0.52</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>99.63</strong></td>
</tr>
</tbody>
</table>

4.3 Morphological and topographic characterisation of the untreated coal fly ash sample

The morphology of the analysed coal fly ash sample, observed from SEM, is shown in Figure 4.3. The particle shape and distribution of the fly ash is reported to be spherical or “ball-bearing” with some of the particles seen to be tightly attached to each other, forming agglomerates. These characteristics are clearly visible in the micrograph.
The spherical nature of the particles was also observed on the TEM micrographs (Figure 4.4) clearly showing the agglomerates formed by the particles.
4.4 FTIR and Raman spectroscopic analysis of untreated Lethabo fly ash

4.4.1 FTIR spectroscopy

A summary of FTIR wavenumber assignments relevant to this study is presented in Table 4.3.

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment [Voll, 2002]</th>
</tr>
</thead>
<tbody>
<tr>
<td>~1055</td>
<td>Si-O asymmetric stretch, mullite, glass, quartz</td>
</tr>
<tr>
<td>902</td>
<td>Al-O stretch, out-of –plane, mullite</td>
</tr>
<tr>
<td>828</td>
<td>Al-O stretch, in-plane, mullite</td>
</tr>
<tr>
<td>773, 795</td>
<td>Asymmetric bend (Si-O-Si), quartz,</td>
</tr>
<tr>
<td>670</td>
<td>Al-O-Al bend , mullite</td>
</tr>
<tr>
<td>584</td>
<td>Al-O stretch, mullite</td>
</tr>
<tr>
<td>462</td>
<td>Symmetric bend (Si-O-Si, Al-O-Al)</td>
</tr>
</tbody>
</table>

The mid-infrared transmission spectrum, shown in Figure 4.5, recorded in an ATR diamond cell is characterised by a broad band between 500-1100 cm\(^{-1}\). The spectrum is a superimposition of the FTIR spectra of silica glass, mullite and a small contribution of \(\alpha\)-quartz (see flyash composition, Table 4.1). In the insert, the 500-1100 cm\(^{-1}\) region is enlarged in order, to distinguish between the small bands that are superimposed on the broad band.
The FTIR spectra of α-quartz and silica glass are shown in Figure 4.6 for comparison purposes and it is clear that both the spectra exhibit broad peaks around 1000 cm\(^{-1}\), peaks in the region 600-800 cm\(^{-1}\) and a prominent peak at ~460 cm\(^{-1}\). The exact position of the peaks depends on the degree of crystallinity and percentage of aluminium present. The FTIR spectrum of mullite has peaks at 1168, 1131, 988, 909, 828, 737, 602, 578 and 482 cm\(^{-1}\). It is clear that many of the peaks in the spectrum of fly ash overlap with that of glass and quartz.

The strongest peak in the fly ash spectrum observed around 1000 cm\(^{-1}\) is attributed Si-O-Si asymmetric stretching vibrations and has contributions of glass, mullite and quartz. The band at 902 cm\(^{-1}\) is attributed to Al-O symmetric stretching vibrations from mullite [Voll, 2002 and Fernández - Jiménez, 2005].

Al-O-Si symmetrical stretching vibrations occur at about 770 cm\(^{-1}\)[Vempati, 1994; Chindaprasirt, 2009] and overlaps of the very characteristic doublet of quartz at 778 and 792 cm\(^{-1}\), which can be distinguished in the insert. The peak at 670 cm\(^{-1}\) has contributions from
quartz and Al-O-Al bending vibrations from mullite. The 584 cm\(^{-1}\) peak belongs to Al-O stretching vibrations (mullite) and the 462 cm\(^{-1}\) peak to symmetric bending vibrations of Si-O-Si and Al-O-Al.

![Figure 4.6: FTIR spectra of glass (bottom) and quartz (top).](image)

A reflectance spectrum, recorded with the Hyperion microscope attached to the FTIR instrument, of the untreated fly ash (Figure 4.7) was also recorded as in reflectance mode the vibrations on the surface of a sample are enhanced. The spectra were recorded between 850 and 4000 cm\(^{-1}\) as the KBr windows of the microscope cut off infrared radiation below 850 cm\(^{-1}\). The broad band representing Si-O stretch vibrations is clearly visible between 900 and 1400 cm\(^{-1}\) and two extra features can be seen. The broad peak between 3000-3500 cm\(^{-1}\) belongs to water (probably adsorbed on the surface) and the two sharp peaks (2860, 2845 cm\(^{-1}\)) to carbon dioxide and originates from CO\(_2\) from the atmosphere.
Raman spectroscopy was used to identify compounds, as well as to study changes in chemical bonding that might have taken place during treatments. In order to obtain a picture of the spatial distribution of the samples, 2D mapping of the samples was undertaken.

### Table 4.4: Main peaks in Raman spectra of components found in fly ash [Voll, 2002; and Schneider, 2005]

<table>
<thead>
<tr>
<th>Component</th>
<th>Wavenumber / cm(^{-1}) positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-quartz</td>
<td>462 (vs), 358 (sm), 206 (m)</td>
</tr>
<tr>
<td>Mullite</td>
<td>1104, 965 (vs), 408, 304,</td>
</tr>
<tr>
<td>Rutile (high temperature)</td>
<td>613 (s), 430 (vs), 258 (s), 153 (sm)</td>
</tr>
<tr>
<td>Alumina silica glass</td>
<td>~480 (br), ~1000 (br)</td>
</tr>
<tr>
<td>CaSO(_4)</td>
<td>1002 (vs)</td>
</tr>
<tr>
<td>CaPO(_4)</td>
<td>961 (vs)</td>
</tr>
</tbody>
</table>
The Raman mapping of the fly ash samples were performed with a WiTec Alpha 300 RA Raman spectrometer. From the 2D array of approximately 10 000 Raman spectra recorded from the sample, five different spectra could be identified. These spectra are presented in Figure 4.8 and wavenumber assignments for each component given in Table 4.4. For easier viewing of the spectra, an offset was added to each spectrum. The images in Figure 4.8 reflect the distribution of the various materials within the analysed sample area. Arrows from the spectrum to the image indicate which spectrum corresponds to which image.

**Figure 4.8: Raman spectra of untreated fly ash at different analysis points**

Spectrum 1 (red) is of α-quartz crystallites with the strongest peak at 462 cm⁻¹. In spectrum 2 (purple) the quartz peak at 462 cm⁻¹ is also visible, with a triplet appearing at 860, 955 and 1008 cm⁻¹. These peaks can be attributed to phosphates and sulphates, but the absence of any crystalline phases of these materials in the XRD data makes it more likely to be an intermediate phase of mullite. It has been shown that the mullite Raman spectrum can vary
considerably depending on the temperature of formation and other materials such as TiO$_2$ present in the sample [Shoval, 2001].

The bands in spectrum 3 (green) are broad and not very intense which is typical for a glass. The Raman spectrum of mullite has its strongest peaks around 304, 408 and 965 cm$^{-1}$ [Shoval, 2001]. The 408 cm$^{-1}$ peak overlaps with the first peak of an alumina/silicate glass representing Si-O bending vibrations at approximately 480 cm$^{-1}$, the spectrum is therefore a superimposition of various amorphous phases of mullite and silica glass.

In contrast the very strong bands of rutile, the high temperature phase of TiO$_2$, can be observed in spectrum 4 (aqua). The Raman cross-section of rutile is very large and therefore a strong Raman signal is obtained, even though rutile is only present in small quantities (see Table 4.2). The last spectrum (blue) with a strong band at 965 cm$^{-1}$ and smaller peaks at 304 and 408 cm$^{-1}$ can be attributed to mullite. These results are summarised in Table 4.4.

The images were then coloured in the colours of the spectra and overlaid into one colour coded image as shown in Figure 4.9. Mixed phases appear as mixed colours in the Raman image. The spectra were normalized to the maximum Raman peak for each component. It is clear from the image that the main phase of the fly ash is amorphous silica glass and amorphous mullite (green).
It also shows that crystalline quartz (red) is embedded in the spheres, but as separate crystallites. Rutile (aqua) is also not homogenously distributed, but interestingly enough the image is spherically shaped and probably formed a layer around one of the glass spheres. Crystalline mullite (blue) is also sparse. It has been observed that nano-mullite crystals are not easily observed with Raman spectroscopy and only larger particles can be detected.

### 4.5 Thermogravimetric analysis of untreated Lethabo fly ash

The results obtained from TGA-IR analyses of the untreated fly ash sample are presented in Figure 4.10. The temperature range studied was chosen in consideration of the decomposition temperature of pure sodium lauryl sulphate (SLS). This will be discussed in more detail in the next chapter.

A very small weight loss percentage (0.1%) was observed for the untreated fly ash over a temperature range of 25 to 400 °C. The weight loss can be ascribed to the loss of moisture and
the onset of oxidation of residual coal present in low percentages in the fly ash. This was confirmed by the occurrence of a CO\textsubscript{2} band in the FTIR of the decomposition gas, taken at 288 °C. However, most of the residual coal trapped in the glass matrix will oxidise at temperatures exceeding 400 °C and this peak probably originates from carbon close to the surface of the glass spheres. The low weight loss observed from the TGA-FTIR is in agreement with the low loss of ignition that was observed on the XRF analysis.

FTIR spectra of the decomposition products were acquired at regular time intervals throughout the thermal measurement performed in the TGA. No other decomposition products were observed within the detection limits of the instrument.

4.6 Particle size distribution

Particle size distribution data for the untreated fly ash sample is presented in Figure 4.11. The lognormal distribution curve indicates that most of the particles in the fly ash sample have a particle size of approximately 10 microns. The fly ash that was analysed was industrially classified as over 90% of the material having a particle diameter of less than 15 microns; hence the particle size distribution indicates the existence of agglomeration of the particles which leads to the great number of large particles.
The phase characteristics of untreated South African Lethabo fly ash were obtained by using a number of analytical techniques. XRD analysis has shown that 62% of the fly ash is in the amorphous glass phase, and that the main crystalline phases are mullite and quartz. The chemical composition as determined by XRF analysis has confirmed that this is a Class F fly ash, with low CaO content.

The spherical morphology and small particle size of the fly ash may enhance its applicability as filler in polymers. TEM analysis has indicated that this sample has a relatively smooth surface topography, with few agglomerates on its surface.

The phases detected in the Raman and FTIR spectra are in line with the XRD data, and the Raman image that was generated with the Raman spectra gives a good spatial representation of the distribution of the different phases in the sample.

**Figure 4.11:** Particle size distribution of untreated Lethabo fly ash

### 4.7 Conclusion

The phase characteristics of untreated South African Lethabo fly ash were obtained by using a number of analytical techniques. XRD analysis has shown that 62% of the fly ash is in the amorphous glass phase, and that the main crystalline phases are mullite and quartz. The chemical composition as determined by XRF analysis has confirmed that this is a Class F fly ash, with low CaO content.

The spherical morphology and small particle size of the fly ash may enhance its applicability as filler in polymers. TEM analysis has indicated that this sample has a relatively smooth surface topography, with few agglomerates on its surface.

The phases detected in the Raman and FTIR spectra are in line with the XRD data, and the Raman image that was generated with the Raman spectra gives a good spatial representation of the distribution of the different phases in the sample.
The sample showed a very low weight loss for temperatures between 25 and 400 °C. This can be an added advantage when using fly ash as filler in polymers because the filler will be thermally stable with low volatility at general polymer processing temperatures.

4.8 Reference


CHAPTER 5
SURFACTANT TREATMENT OF FLY ASH SAMPLES

5.1 Introduction

Surface treatment is a principal method applied to change the wetting behaviour of mineral or inorganic fillers. Surfactants are generally used as surface modifiers to increase the hydrophobicity of the surface of hydrophilic inorganic fillers, which consequently increases compatibility between the polar inorganic and non-polar organic matrices.

Nath [2010a and b] have shown how the surface of Australian fly ash can be modified by sodium lauryl sulphate (SLS), and the resulting fly ash was used as filler in composite films with polyvinyl alcohol (PVA). They then compared the properties of the 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 (2001) modified silica nanoparticles by using a cationic surfactant-CTAB. Optimal conditions were discussed, and the combined results of FTIR, 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 upon treatment, and that the better dispersal state of CTAB-modified silica nanoparticles will be advantageous when used as a filler in polymeric materials.

In this chapter, the effect of an anionic surfactant (sodium lauryl sulphate) on the surface and physical properties of South African coal fly ash is investigated, and the resultant products are then characterised.

Fly ash was initially treated for 18 and 66 hours and after considering the results the time was reduced to 6 hours under the conditions described in Chapter 3. Two temperature conditions were investigated for each period of exposure of the fly ash sample to the surfactant.
5.2 Sodium Lauryl Sulphate (SLS)

Sodium Lauryl Sulphate (SLS) also known as Sodium dodecyl Sulphate (SDS) is an anionic surfactant that consists of a 12-carbon chain and a sulphonate head group. Its chemical and structural formula are given in Figure 5.1. The sulphonate group of the SLS is negatively charged and polar and acts as the hydrophilic part of the surfactant while the 12-carbon chain is non-polar and acts as the hydrophilic part.

\[
\text{Figure 5.1: Chemical and structural formula of Sodium Lauryl Sulphate}
\]

\[
\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}
\]

SLS is mainly used in cosmetics and industrial chemicals as a detergent which is supported by its anionic nature. It is a widely used, affordable and easily accessible surfactant, rendering it suitable for application in the surface treatment of fly ash.

5.3 Results and Discussion

5.3.1 XRD and XRF results

The phase composition of the 2.0 % SLS treated fly ash sample, reported in Figure 5.2 and Table 5.1, do not differ significantly from those of the untreated fly ash sample, Figure 4.1 and Table 4.1. Mineral phases were found to be similar for the two fly ash samples. The bulk phase composition of the treated fly ash was not affected by the SLS treatment.
The same observations were made for the fly ash treated at 50 °C for 6, 18 and 66 hours as well as for the 80 °C 6 and 66 hours treatment conditions. The concentration of the SLS, considering different treatment time and temperature, did not affect the chemical composition of the obtained fly ash products.

Table 5.1: XRD quantitative results of untreated fly ash (FA) and 2.0% SLS treated fly ash sample at 80 °C for 18 hours (18hrs SLS) values are reported as weight percentage

<table>
<thead>
<tr>
<th>Phase</th>
<th>FA</th>
<th>18hrs SLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous</td>
<td>62.1</td>
<td>62.8</td>
</tr>
<tr>
<td>Mullite</td>
<td>31.8</td>
<td>31.1</td>
</tr>
<tr>
<td>Quartz</td>
<td>6.2</td>
<td>6.1</td>
</tr>
</tbody>
</table>
Figure 5.2: XRD spectrum of 2.0% SLS treated fly ash sample treated for 18 hours at 80 °C.

- Position [°2Theta] (Cobalt (Co))
- Counts
- Lethabo_FA-Sls + Si
- Peak List
  - 01-079-1457; Mullite, syn; Al4.52 Si1.48 O9.74
  - 01-078-1252; Quartz low, syn; Si O2
  - 00-027-1402; Silicon, syn; Si
The elemental analyses of the fly ash sample treated with 2% SLS at 6 hours obtained from the XRF analyses are summarised in Table 5.2. The sample was found to contain higher moisture content, observed from the increased loss on ignition value in comparison to that of the untreated fly ash sample.

The percentage composition of CaO in the treated ash sample was found to be slightly lower than that of the untreated ash. The CaO content of fly ash influences its hydration, and a decrease in CaO content may also decrease the hydrophilicity of the ash [Ćojbašić, 2005]. A significant decrease was observed in the iron content after the aqueous SLS treatment, indicating that both calcium and iron leached into solution.

Table 5.2: XRF chemical composition of untreated fly ash (FA) and of 2.0% SLS treated fly ash sample at 80 °C for 6 hours (6 h SLS), values are reported as weight percentage.

<table>
<thead>
<tr>
<th>Compound</th>
<th>FA</th>
<th>6h SLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.3</td>
<td>52.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.01</td>
<td>1.71</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>34.0</td>
<td>34.1</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.78</td>
<td>3.08</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.99</td>
<td>1.31</td>
</tr>
<tr>
<td>CaO</td>
<td>5.06</td>
<td>4.30</td>
</tr>
<tr>
<td>Na₂O</td>
<td>&lt;0.01</td>
<td>0.11</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.87</td>
<td>0.92</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.59</td>
<td>0.68</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.07</td>
<td>0.03</td>
</tr>
<tr>
<td>NiO</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>0.52</td>
<td>2.23</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>99.39</strong></td>
<td><strong>100.64</strong></td>
</tr>
</tbody>
</table>
5.3.2 Scanning Electron Microscopy

It seems that the particle distribution of the SLS treated fly ash samples changed in comparison to that of the analysed raw fly ash sample. Untreated fly ash particles were observed to be closely packed together forming a considerable amount of agglomerates, as explained in Chapter 4. The particles of the treated fly ash (Figure 5.3) are spread out, and many of the large agglomerates were broken down by the interaction of the SLS with the fly ash sample.

![Untreated fly ash sample](image1)  ![SLS treated fly ash sample](image2)

**Figure 5.3: SEM monograms of untreated and SLS treated fly ash**

Better particle separation was observed for all temperature conditions. The degree of agglomeration is reduced in the treated fly ash resulting in well separated particles. This occurs mostly for the 0.5% and the 2.0% SLS treated FA samples. The 0.1% SLS treated sample also shows a reduction in agglomeration as well particle separation, although to a lesser extent.

The water treated samples also have a slight reduction in agglomeration which could be due to mechanical action. The samples were subjected to vigorous shaking during treatment. Figure 5.4 shows the same trend of reduction of agglomeration and increase in particle separation.
Comparing the 2.0% SLS treated samples for 6, 18 and 66 hours at 80 °C respectively (Figure 5.5) the difference in particle separation can be clearly observed. The micrographs show that for the same concentration of SLS and the same temperature the exposure period is important. The 6 hours treated samples show a higher degree of particle separation and smaller degree of agglomeration when compared to the 18 and 66 hours treated samples.

This effect can possibly be explained by any of the following reasons, but further investigations are necessary for clarification. Wolff [1992] reported that the presence of silanol groups on the surface of silica, used as filler in rubber, will cause strong filler-filler interactions leading to agglomeration of the filler in a rubber matrix. Prolonged exposure of the fly ash to water will cause hydroxylation of the fly ash surface, which may lead to increased agglomeration of fly ash particles.
On the other hand, the stability of SLS solutions has been studied by Sugàr et al [1999], who reported that these solutions will degrade with time, and that fresh solutions need to be prepared on the day of use. It is possible that the SLS solutions decayed during treatment leading to a decrease in separation of agglomerates.

When considering temperature conditions, the extent of particle separation was seen to be greater for the samples treated at 80 °C than those treated at 50 °C. FTIR results, still to be discussed, indicate a significant change in characteristics of the fly ash samples after treatment.
5.3.3 Effect of SLS treatment on the particle size distribution of fly ash

Particle size distribution data was obtained for the untreated and SLS treated fly ash samples. The results obtained for all treated samples were similar, irrespective of the treatment conditions. A representation of the plotted data is given in Figure 5.7 for the samples treated with SLS for 6 hours at 80 °C in comparison to the plotted data of untreated fly ash.
The median particle size decreased upon treatment, with a corresponding reduction in the frequency (volume %). The shape of the lognormal distribution curves are wider towards smaller particle size fractions for the treated samples compared to that of the untreated fly ash, indicating that the amount of smaller particles have increased upon treatment. This supports the results obtained from the SEM, indicating smaller particles and less agglomerates for the treated samples.

![Graph of lognormal size distributions](image)

**Figure 5.8: Comparison of the lognormal size distributions of untreated fly ash, and samples treated in distilled water and SLS for 66 hours at 80 °C**

Although the shape of the lognormal distribution curves were similar, for the 66 hours treatment, as seen in Figure 5.8, a small fraction of particles with a size above 100 microns was observed, indicating increased agglomeration for the 0.5 and 2.0% SLS treated samples. This effect was not observed for the fly ash treated in a 0.1% SLS solution. These results confirm the SEM results, shown in Figure 5.5, where a higher degree of agglomeration for the 66 hours treated samples was observed.
5.3.4 FTIR and Raman spectroscopic analysis of the treated fly ash samples

FTIR and Raman spectra of pure SLS, \((\text{CH}_3\text{(CH}_2)_{11}\text{OSO}_3\text{Na})\), were acquired and are presented in Figures 5.9 and 5.10. The FTIR spectrum shows the presence of water in the sample through the OH stretching bands at approximately 3500 cm\(^{-1}\) and bending vibrations at 1645 cm\(^{-1}\). Table 5.3 lists the vibrational frequencies of the functional groups (long aliphatic chain and \(\text{SO}_4\)) group present in SLS.

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2936, 2848</td>
<td>(\text{CH}_3) asymmetric and symmetric stretching</td>
</tr>
<tr>
<td>2914, 2845</td>
<td>(\text{CH}_2) asymmetric and symmetric stretching</td>
</tr>
<tr>
<td>~3600 (br)</td>
<td>OH stretching, water</td>
</tr>
<tr>
<td>1600</td>
<td>OH bending, water</td>
</tr>
<tr>
<td>1440</td>
<td>bending (\text{CH}_2)</td>
</tr>
<tr>
<td>1380</td>
<td>(\text{CH}_3) bending</td>
</tr>
<tr>
<td>1050</td>
<td>C-C stretching</td>
</tr>
<tr>
<td>1080-1180 and 1370-1420</td>
<td>Asymmetric and symmetric stretch of (\text{SO}_3)</td>
</tr>
<tr>
<td>600-1300</td>
<td>C-C aliphatic chain</td>
</tr>
<tr>
<td>1000-1300</td>
<td>C-O Ester Stretch</td>
</tr>
<tr>
<td>1000-1300</td>
<td>C-O Ester Stretch</td>
</tr>
</tbody>
</table>

The CH asymmetric stretching bands is observed at 2936 cm\(^{-1}\) (\(\text{CH}_3\)), 2914 cm\(^{-1}\) (\(\text{CH}_2\)) and the symmetric stretch vibrations at 2848 cm\(^{-1}\) (\(\text{CH}_3\)) and 2845 cm\(^{-1}\) (\(\text{CH}_2\)). The 1466 cm\(^{-1}\) peak represents the bending vibrations of the \(\text{CH}_2\) chain. The skeletal structure (C-C) of the surfactant is observed at 1215, 1237 and at 630 cm\(^{-1}\). SLS is characterised with organic sulphates at 1087 cm\(^{-1}\).
Figure 5.9: FTIR spectrum of Sodium Lauryl Sulphate

Figure 5.10: Raman spectrum of Pure SLS taken at two wavenumber ranges
The most intense bands in the SLS Raman spectrum belong to CH stretching vibrations, similar as in the FTIR spectrum. The CH\textsubscript{2} stretching band was observed at approximately 2882 cm\textsuperscript{-1} with the CH\textsubscript{2} band at 2847 cm\textsuperscript{-1}.

The treated fly ash samples of all treatment conditions were analysed with FTIR and some with Raman spectroscopy.

![FTIR spectra of treated FA samples at 50 °C for 18 hours, untreated FA and pure SLS](diagram)

**Figure 5.11:** FTIR spectra of treated FA samples at 50 °C for 18 hours, untreated FA and pure SLS

For the 18 hours treated fly ash samples, SLS corresponding peaks were observed between 1200 and 1400 cm\textsuperscript{-1} on the 0.1 %, 0.5% and 2.0 % SLS treated sample, shown in Figures 5.11 and 5.12. CH bands were observed for samples treated at both 50 and 80 °C. The same peaks also occurred in spectra of the 66 hours treatment sample at both treatment temperatures.
Figure 5.12: FTIR spectra of treated FA samples at 80 °C for 18 hours, untreated FA and pure SLS

Extra SLS corresponding peaks, indicated by an arrow on the spectra in Figure 5.13, were observed for the 6 hours treated samples compared to the 18 and 66 hours treated samples. These peaks were observed for the 2.0% SLS treated samples for both temperature treatment conditions, and were found to be more prominent for the 80 °C treatment temperature as shown below in the respective temperature FTIR spectra, Figures 5.13 and 5.14. The pure SLS as well as the raw fly ash spectra were included for comparison.
The spectrum of the fly ash treated with the 2.0% SLS solution show peaks on the spectrum that correspond to those present in the FTIR spectrum for pure SLS. The SLS spectrum is characterised by peaks that represent a CH$_2$ bending band at 1468 cm$^{-1}$ and CH stretching vibration bands at 2917 and 2850 cm$^{-1}$. The corresponding peaks on the 2.0% SLS treated fly ash sample were observed at 1476, 2933 and 2836 cm$^{-1}$ respectively, Figure 5.14.

Comparing the FTIR spectra obtained at 50 °C to those obtained at 80 °C, not much difference was observed. However, the peaks on the 2.0% SLS treated fly ash sample were more prominent and could easily be correlated to those of the SLS sample. The peaks on the 2.0% SLS treated fly ash sample spectrum were observed at 1476, 2921 and 2855 cm$^{-1}$ respectively. Two more peaks were observed and were characteristic to the skeletal vibration of the SLS. These were found to be positioned at 1237 and 1215 cm$^{-1}$ for pure SLS while for the 2.0% SLS treated fly ash sample they were positioned at 1224 and 1192 cm$^{-1}$ respectively.

Figure 5.13: FTIR spectra of treated FA samples at 50 °C for 6 hours, untreated FA and pure SLS
The observed peaks on the treated fly ash sample were found to be relatively at the same positions for the different treatment temperatures, but the intensities of the peaks differed with those at 80 °C being more prominent. This could indicate that there isn’t much difference in bonding patterns that might exist between the fly ash particles and the SLS.

In Figure 5.15, small sharp peaks at the exact positions of the SLS bands are clearly visible in the spectrum of the 2.0% SLS modified fly ash. A closer look (see insert) shows that the peaks at 1248 and 1216 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 would explain the hydrophobic behaviour observed in the contact angle experiments, still to be discussed, and is also in line with the shape of the agglomerates observed in the TEM monographs.
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.

![Figure 5.15: Comparison of FTIR spectra of pure SLS, untreated fly ash, and 2.0% SLS treated fly ash for 6 hours at 80 °C](image)

Figures 5.16 and 5.17 represent the Raman spectra of the 2.0% SLS treated Fly ash sample at 80 °C for 6 hours. For better viewing and band assignment Figure 5.17 was adapted from Figure 5.16, with a magnification of the section that contains bands. The spectra were acquired on different sites of the sample as shown in Figure 5.17. The composition of fly ash is heterogeneous and that can be seen in the treated sample as well. For the different spectra, different peaks were observed.
Figure 5. 16: The different Raman spectra of 2.0% SLS treated fly ash at 80 °C for 6 hours obtained during 2D scanning of a small area of flyash.

Figure 5. 17: Raman spectra of 2.0% SLS treated fly ash at 80 °C for 6 hours using different analysis sites shown.
Using the table in Chapter 4, spectrum (a) is of silica-aluminium glass, spectrum (b) belongs to α-quartz, spectrum (c) to TiO₂ (anatase phase) and spectrum (d) to mullite [Schneider, 2005 ]. As from the untreated fly ash the glass component is the main phase present. Quartz, mullite and the titanium dioxide phases are randomly spaced and in most instances adsorbed on the surface of spherical glass particles.

![Figure 5.18: Comparison of Raman spectra of pure SLS and 2.0% SLS treated fly ash for 6 hours at 80 °C](image)

**5.3.5 Topography of the SLS modified fly ash**

The TEM images, Figures 5.19 and 5.20, show agglomerates on the surface of the treated fly ash spheres. There is a distinct difference between the morphology of the agglomerates on the untreated and SLS treated fly ash samples. The agglomerates on the untreated fly ash spheres are considerably less than those on the SLS treated fly ash, and have a less ordered spherical structure. Another interesting observation, which has been confirmed by the results obtained from the FTIR and Raman measurements, is that not all SLS modified fly ash particles were covered with agglomerates to the same degree.
Some fly ash particles had a low degree of coverage, while others were covered extensively as was observed on the SEM monographs in earlier figures. Also, the needle-like shape of the agglomerates on the SLS treated fly ash was different from that of the agglomerates observed on the untreated and distilled water treated fly ash sample’s surfaces, which were more rounded in shape.

Both Chen et al [2005] and Hower et al [2008] have described the occurrence of carbonaceous agglomerates on different types of fly ash particles. Chen performed a TEM study on ultrafine fly ash, and described the morphologies of soot aggregates on the fly ash surface to have branching chain-like structures. The typical particle size of these aggregates was in the region
of 20-50 nm. The micro textures of these soot particles were described as consisting of concentrically stacked graphitic layers. These results were confirmed by Hower [2008], who described the soot particles to have a “fullerene-like nanocarbon with concentric ring-structure”.

However, the morphology of the agglomerates described by these authors was distinctly different from the needle-like agglomerates observed on the surface of the SLS modified fly ash in this study.

5.3.6 Thermogravimetric Analysis of SLS modified fly ash

The TGA curve of pure SLS (Figure 5.21) shows a small weight loss corresponding to the loss of water between 100 and 200 °C. This confirms the FTIR results for pure SLS, discussed earlier in the chapter, where a broad band corresponding to the occurrence of water was observed in the FTIR spectrum.

Between 200 and 300 °C, a significant weight loss occurred with a corresponding evolution of CO$_2$, sulphates and hydrocarbons from the sample. The FTIR spectrum of the gaseous decomposition product, taken at 288 °C is shown in Figure 5.21. Characteristic peaks of the aliphatic chain of SLS are observed at approximately 1438 and 2930 cm$^{-1}$ for bending and stretching CH$_2$ bands respectively. The CO$_2$ band was prominent at 2346 cm$^{-1}$ with that of the inorganic sulphate noted at approximately 1165 cm$^{-1}$.

The occurrence of CO$_2$ as decomposition product of pure SLS is possibly due to oxidation of the alkyl chain. These measurements were performed in an air atmosphere. Sreedhar [2006] has also reported the occurrence of CO$_2$ upon thermal decomposition of SLS-doped polyaniline between 260 – 600 °C, as studied by TGA-MS.
The results obtained from TGA-FTIR analyses of the SLS modified fly ash sample are presented in Figure 5.22. Since SLS decomposes in the region 200-300 °C, TGA-FTIR measurements of the treated fly ash samples were performed only up to 400 °C. FTIR spectra of the decomposition products were acquired at regular time intervals throughout the thermal measurement performed in the TGA.

Thermal analysis of SLS modified fly ash sample was different from that of the untreated fly ash, which was reported in Chapter 4. A significant weight loss was observed over the temperature range 200 to 250 °C, and two different decomposition products were observed from the FTIR data.

Firstly, C-H stretching vibrations was observed and was found to be strongest at a corresponding TGA temperature of 236 °C, which is consistent with the 0.4% weight loss observed at this temperature. This decomposition product can be ascribed to the presence of hydrocarbons originating from the SLS in the modified fly ash sample.
Secondly, the vibrational bands of CO$_2$ were also observed over a wide temperature range, and were found to be strongest at 319 °C. This can be ascribed to the onset of oxidation of residual coal within the fly ash as well as the decomposition product of the SLS that might be on the surface of the fly ash particles.

Sicard [2001] studied the thermal decomposition of SLS from mesoporous alumina by sample controlled thermal analysis. His study has shown that thermal decomposition of pure SLS commences at 200 °C, and that the alkyl chain will be removed first. The sulphate head group is removed thereafter. The author noticed that SLS interacting with the alumina will be thermally more stable due to strong interactions between the sulphate head group and the alumina surface, causing an increase in the decomposition temperature of the sulphate group from the alumina surface. The temperature at which the alkyl chain is lost from the alumina surface decreased in comparison to that of the pure SLS. Due to the small amount of SLS adsorbed on the surface of the fly ash, this could not be confirmed in this study.
The TGA-FTIR results confirmed the presence of SLS on the surface of the treated samples which correspond to the TEM results. The TGA-FTIR results also confirm the FTIR results that were obtained for the treated samples showing an occurrence of SLS corresponding vibrational bands as well as a shift in the position of the CH bands.

5.3.7 Contact angle measurements

The hydrophobicity of a solid material can be determined by contact angle measurements [Lazghab, 2005]. Contact angle can be defined as the measure of the ability of a liquid to disperse on a surface. Water gives an excellent indication of hydrophobicity of a solid material if used as the testing liquid. A contact angle of less than 90° indicates a hydrophilic surface while that greater than 90° indicates a hydrophobic surface.

The contact angle of untreated fly ash and the 2.0% SLS treated fly ash at 80 °C for 6 hours was measured using water as the testing liquid. Untreated fly ash was found to be hydrophilic with an initial contact angle of approximately 32°. The treated fly ash has shown an initial contact angle of 137°, indicating a very hydrophobic surface. Figure 5.23 shows the ability of a water droplet to disperse on the two fly ash samples.

![Figure 5.23: Photographs of water droplets deposited on surfaces of a fly ash powder bed, taken 1 s after deposition](image)

Untreated fly ash  
2.0% SLS treated fly ash
5.4 Conclusion

Although the phase and chemical composition of the SLS modified coal fly ash samples was not altered extensively, significant changes could be observed in its physical properties. An increased loss on ignition value in comparison to that of the untreated fly ash sample was noted from the XRF result of the 2.0% SLS treated ash sample.

Particle distribution of the SLS treated fly ash samples changed in comparison to that of the analysed raw fly ash sample, implying better particle separation for the treated samples. The median particle size of the fly ash samples decreased upon treatment.

The occurrence of agglomerates on the surface of the SLS modified fly ash seen on the SEM was confirmed by TEM. The TGA showed a significant weight loss over the temperature range of 230 to 250 °C, and two different decomposition products were observed from the FTIR data, CH₂ and CO₂. The decomposition products can be ascribed to the presence of hydrocarbons originating from the SLS in the modified fly ash sample and the onset of oxidation of residual coal within the fly ash.

The possibility of interactions between fly ash and SLS could be deduced from the FTIR results, where a small shift in peak positions of the S-O stretch was observed. This may be indicative of electrostatic interactions rather than bonding interactions between SLS and fly ash. The peaks corresponding to C-H groups of SLS, observed on the treated samples, did not display a shift. This could point to interaction of the SLS to the surface of the fly ash being through the sulphate anion, implying that the hydrocarbon chain is aligned outwards from the fly ash kernel. In contrast to FTIR, the presence of SLS could not be observed with Raman spectroscopy.

In comparison to the untreated fly ash, the 2.0% SLS treated fly ash was found to be hydrophobic with an initial contact angle of 137°.
5.5 References

CHAPTER 6
COUNTER ION EFFECT ON SURFACTANT AGGREGATION

6.1 Introduction

Counter ions have been reported to have an influence on the interaction of surfactants with a variety of surfaces [Bitting, 1985]. The presence of a counter ion in a surfactant solution increases the chances of surfactant aggregate formation. Surfactant adsorption can also be enhanced below the stated c.m.c of the surfactant [Atkin, 2003b].

Surfactant counter ions can alter the hydrophilicity of a surface as well as it hydrophobic interactions with aggregates that form on the surface [Silbert, 2010]. Enhanced surfactant adsorption can lead to a decrease in the hydrophilic nature of a surface due to the change of its morphology after surfactant adsorption [Atkin, 2003b]. Ion binding in a surfactant solution is increased by the presence of a counter ion, influencing the extent of surfactant adsorption and micelle formation [Umlong, 2006].

6.2 Experimental

Solutions of NaCl and KIO$_3$ with a concentration of 0.1 M were prepared separately. The solutions were used to prepare a salt-surfactant solution. SLS was dissolved in the salt solution to obtain concentrations of 0.1, 0.5 and 2.0% of the SLS. Salt solutions without any added surfactant were used as controls to determine their effect on the fly ash surface. The salt-surfactant solution was then used to treat fly ash samples as mentioned in Chapter 3. All samples were treated at 80 °C for 6 hours.
6.3 Results and Discussion

6.3.1 XRF

No significant changes were observed on the chemical composition of the treated fly ash samples, as presented in Table 6.1.

Table 6.1: XRF chemical composition of untreated fly ash (FA), KIO₃-SLS and NaCl-SLS treated fly ash for 6 hours; values are reported as weight percentages.

<table>
<thead>
<tr>
<th>Compound</th>
<th>FA</th>
<th>KIO₃</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>49.3</td>
<td>51.0</td>
<td>52.2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.01</td>
<td>1.7</td>
<td>1.71</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>34.0</td>
<td>33.3</td>
<td>34.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.78</td>
<td>3.02</td>
<td>3.08</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.99</td>
<td>1.27</td>
<td>1.32</td>
</tr>
<tr>
<td>CaO</td>
<td>5.06</td>
<td>4.20</td>
<td>4.28</td>
</tr>
<tr>
<td>Na₂O</td>
<td>&lt;0.01</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.87</td>
<td>1.1</td>
<td>0.93</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.59</td>
<td>0.66</td>
<td>0.68</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.07</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>NiO</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.08</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>CuO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>0.52</td>
<td>3.66</td>
<td>1.70</td>
</tr>
<tr>
<td>TOTAL</td>
<td>99.4</td>
<td>100.2</td>
<td>98.9</td>
</tr>
</tbody>
</table>

6.3.2 Scanning Electron Microscopy

SEM analysis of the treated samples, Figure 6.1, showed that the particles treated with 0.1 M KIO₃ solution seem to have formed more agglomerates with each other. When compared to the particles of the untreated fly ash, the 0.1 M KIO₃ treated fly ash particles were not significantly different. As the concentration of the SLS increases particle separation seems to be more prominent and particle coating is observed on the surface of some of the particles (Figure 6.2).
Figure 6.1: SEM images of fly ash samples treated at 80 °C for 6 hours

Figure 6.2 shows the coating observed on some of the fly ash particles treated with KIO₃–0.5% SLS and KIO₃–2.0% SLS solutions. Only a few particles were found to be coated (shown with red arrows) in the KIO₃–0.5% SLS treated sample. More particles were found to have been coated for the KIO₃–2.0% SLS treated sample, with more than one coated particle found in the same area of analysis.

Figure 6.2: SEM images of fly ash samples treated at 80 °C for 6 hours
The particles of fly ash treated with 0.1 M NaCl solution still show the occurrence of agglomerates, yet smaller in comparison to those of untreated fly ash shown in Figure 4.2. Particle separation also increased with increasing concentration of SLS in the salt-surfactant treatment combination.

Figure 6.3: SEM images of fly ash samples treated at 80°C for 6 hours

6.3.3 Transmission Electron Microscopy

The coating observed on the SEM micrographs was confirmed by the TEM micrographs, Figures 6.4 and 6.5. Needle-like shaped aggregates on the surface of the fly ash particles were observed on both salt-surfactant solution treatments for SLS concentrations of 0.5% and 2.0%. The needle-like shaped aggregates were seen to be more prominent for the 2.0% SLS treatment. Most of the fly ash particles were observed to have aggregates on their surface, but not all of them were completely coated.
The extent of coating observed for the SLS–0.1 M KIO₃ treated sample differed for the 0.5% and 2.0% SLS-salt solution treated sample. Less coating was observed on the 0.1% SLS-salt solution treated sample. The coating observed on the 0.5% SLS–0.1 M KIO₃ treated sample is defined needle-like structures while those on the 2.0% SLS–0.1 M KIO₃ is a network of needle-like structures (Figure 6.4). The increased concentration of SLS led to increased coverage and build-up of SLS agglomerated on the fly ash surface.

For the SLS–0.1 M NaCl sample treatment, well defined needle like structures were observed for both the 0.5% and 2.0% SLS–0.1 M NaCl treated samples.
6.3.4 FTIR and Raman spectroscopic analysis

SLS characteristic bands were observed on the treated samples, especially for the 0.5% and 2.0% SLS–0.1 M salts, KIO$_3$ and NaCl, (Figures 6.6 and 6.8). SLS characteristic bands were mainly observed on the 0.5% SLS–0.1 M NaCl treated sample with the 2.0% SLS–0.1 M NaCl having only a few bands, Figure 6.8.

The bands that were observed for this treatment solutions correspond to those observed for the SLS solution treatment, as discussed in Chapter 5, Figure 5.11. A CH$_2$ bending band was observed at 1479 cm$^{-1}$ and two stretching CH$_2$ bands at 2906 and 2841 cm$^{-1}$. Two bands at 1233 and 1206 cm$^{-1}$ representing organic sulphate peaks were also present.
Figure 6.6: FTIR spectra of fly ash samples treated at 80 °C for 6 hours with KIO₃-SLS.

Figure 6.7: Raman spectra of 2.0% SLS-0.1 M KIO₃ treated fly ash at 80 °C for 6 hours at different analysis sites shown.
Figure 6.8: FTIR spectra of fly ash samples treated at 80 °C for 6 hours with NaCl-SLS

Figure 6.9: Raman spectra of 2.0% SLS-0.1 M NaCl treated fly ash at 80 °C for 6 hours at different analysis sites shown
The Raman spectra, represented in Figures 6.7 and 6.9 are very similar to that of the untreated samples. The two broad bands in the green spectrum, (a), represent silica alumina glass and is the main phase in flyash (see Chapter 4). Mullite peaks (spectrum d) are seen on this spectrum at approximately 920 cm\(^{-1}\) with a peak at 408 cm\(^{-1}\) that overlaps with silicate glass peaks (green spectrum). The red spectrum, (b), with the strongest peak observed at 462 cm\(^{-1}\) is of crystalline \(\alpha\)-quartz.

Amorphous carbon was observed on the 2.0% SLS-0.1 M KIO\(_3\) treated sample through the two characteristic peaks at \(~1350\) and \(~1600\) cm\(^{-1}\) in the yellow spectrum (c). The yellow spectrum (c) with peaks at 613, 430 and 258 is rutile, the high temperature phase of TiO\(_2\) (see Table 4.4, Chapter 4).

The presence of SLS was not observed using Raman spectroscopy and is below the detection limits of the Raman instrument used. However, the Raman mapping data rendered interesting information about the spatial distribution of the various phases in the fly ash. The spherical shape of rutile, anatase, mullite and in some instances quartz phases is an indication that these phases form on the surface of the spherical glass particles.

### 6.4 Conclusion

Treatment of fly ash with a salt-surfactant solution did not alter the chemical composition of the ash. The introduction of a counter ion in the surfactant solution increased the aggregation of the surfactant on the surface of the fly ash. The increase of surfactant adsorption led to the decrease in the extent of agglomeration of fly ash particles.

FTIR spectra confirm the presence of surfactant aggregation on the fly ash particles, showing the different phases in the sample as well as sulphates that can be attributed to SLS micelles. Raman spectroscopy was not sensitive enough to detect the organic phase of SLS on the samples.
6.5 References

CHAPTER 7
REFLUX TREATMENT OF FLY ASH

7.1 Introduction

At a concentration of 2.0% of SLS, the surface coverage of fly ash with the surfactant was found to be at its optimum at 80 °C and 6 hours, as reported in Chapters 5 and 6. The objective of this chapter is to investigate the effect of a further increase in temperature and surfactant concentration on the surface coverage onto fly ash.

The reflux treatment introduced an increase in temperature approaching the boiling point of the aqueous surfactant solution. An increase in the temperature of ionic surfactants tends to decrease the c.m.c of a surfactant, leading to an increase in micellisation [Kim, 2003]. This effect is expected to result in increased coverage of the surfactant on the fly ash surface.

7.2 Experimental

A reflux system, as shown in Figure 7.1, was set up for the reflux treatment of fly ash. The aqueous concentrations of SLS used were 0.5%, 2.0% and 4.0% by weight. Distilled water was used as a control for the treatment. The fly ash-SLS mixtures were refluxed at the boiling temperature of the SLS-water solution for 6 hours.

Figure 7.1: Reflux system for surfactant treatment on fly ash
7.3 Results and Discussion

7.3.1 SEM and TEM

The SEM micrographs of reflux samples, shown in Figure 7.2, show agglomeration of the fly ash particles mainly for the sample treated in distilled water. The particles of the 2.0% SLS treatment formed a network of agglomerates. This phenomenon cannot be explained.

![Distilled water](image1.png)  ![0.5% SLS](image2.png)

![2.0% SLS](image3.png)  ![4.0% SLS](image4.png)

Figure 7.2: SEM images of refluxed fly ash samples treated for 6 hours

Particle coating was observed for all the SLS reflux treated samples with a higher degree of surfactant-coverage on the surface of the 2.0% and 4.0% SLS treated fly ash samples compared to the 0.5% SLS treated sample. A great number of particles of these treated samples were found to be coated. The SEM images of the SLS refluxed fly ash samples, taken at higher magnification, are shown in Figure 7.3. These images show an even distribution of the coating of particles as well as the density of the coating, indicating that most of the fly ash particles were coated with the surfactant.
Figure 7.3: SEM images of SLS refluxed fly ash samples at higher magnifications, showing surface coating.

Figure 7.4: TEM images of 2.0% SLS refluxed fly ash samples.

The morphology of the coating on reflux treated fly ash samples was seen to be different from those seen on the 2.0% SLS treated sample at 80 °C for 6 hours. The agglomerates are tighter and thicker and the observation was confirmed by the TEM micrographs shown in Figures 7.4 and 7.5. Figure 7.5 shows the extensive coverage of a particle observed for the 4.0% SLS refluxed sample.
7.3.2 FTIR and Raman Spectroscopic analysis

The reflux treated samples were characterised with broad OH stretching and H$_2$O bending bands at approximately 3300 and 1600 cm$^{-1}$ respectively, Figure 7.6. The presence of SLS corresponding peaks was notable on the spectra, with CH$_2$ stretching bands at approximately 2840 and 2932 cm$^{-1}$, CH$_2$ bending bands at 1460 cm$^{-1}$ and an organic sulphate band which was observed on the 2.0% SLS treated sample at 1141 cm$^{-1}$.

![Figure 7.6: FTIR spectra of refluxed fly ash samples treated for 6 hours](image)
The Raman spectra (Figure 7.7) shows different components present in the treated sample. The red spectrum is characteristic of α-quartz at 462 cm$^{-1}$, the blue spectrum represents mullite with bands at approximately 310, and 945 cm$^{-1}$, with glass being represented by the green spectrum. Sulphates were observed in the red spectrum at approximately 1100 cm$^{-1}$, as well as amorphous carbon.

![Raman spectra and Color coded Raman image]

**Figure 7.7: Raman spectra of 4.0% SLS reflux treated fly ash for 6 hours taken at different analysis sites shown**

### 7.3.3 TGA-FTIR

TGA-FTIR analyses were run for the 4.0% SLS reflux treated sample and the results are represented in Figure 7.8. A continuous weight loss was observed over the studied temperature range, with CH and CO$_2$ being observed on the FTIR spectra of the gaseous decomposition products.
The FTIR results of the decomposition products, Figure 7.8, indicate that the weight loss can initially be ascribed to the decomposition of the SLS from the fly ash surface, followed by oxidation of carbon contained in the fly ash and in the SLS that might on the surface of the fly ash particles thereafter. The vibrational band of CO$_2$ was observed at approximately 2350 cm$^{-1}$ and that of the CH stretch band at approximately 2930 cm$^{-1}$.

![TGA curve of 4% SLS Reflux treated fly ash](image1.png)

![4.0% SLS Reflux for 6 hours](image2.png)

Figure 7.8: TGA-FTIR results obtained for the 4.0 % SLS refluxed fly ash treated for 6hrs

### 7.3.4 Contact angle measurements

The coating on the 4.0% SLS refluxed fly ash sample, as observed on the TEM, changes the surface of the fly ash from hydrophilic to hydrophobic, thus the inability of the water droplet to disperse on the surface, Figure 7.9. The 4.0% SLS refluxed fly ash samples has shown a contact angle of 140°.
7.4 Conclusion

An increase in the temperature treatment of fly ash samples with aqueous surfactant solution resulted in increased surface coverage of the fly ash samples treated with 0.5%, 2.0% and 4.0% surfactant solutions. Kim et al [2003] mentioned that an increase in temperature leads to increased micellisation of a surfactant, which can explain why more extensive particle coverage of the surfactant onto the fly ash surface is observed.

The particle coverage of fly ash with SLS changes its surface from hydrophilic to hydrophobic indicated by the measured contact angles. FTIR spectra show characteristic SLS bands on the treated fly ash samples. A very low weight loss was observed from the TGA-FTIR result for the 4.0% SLS treated samples but could clearly indicate the presence of SLS in the gas phase decomposition product.

7.5 References

CHAPTER 8

FLY ASH – POLY VINYL CHLORIDE

8.1 Introduction

Poly-Vinyl Chloride (PVC) is a polymer made by the catalytic polymerisation of vinyl chloride, with 57% chlorine and 43% carbon [Wiebking, 1998]. It is a strong thermoplastic resin that can be either rigid or flexible and can be softened by heating. The properties of PVC are modified by the addition of plasticisers and fillers and its flexibility can be influenced by the kind of compounds added to it [Bryant, 2002]. Plasticisers have been found to increase the flexibility of PVC products, as well as reduce the difficulty of processing.

PVC is the second most widely used polymer due to its strength, ease of blending and processing, and its fire preventing properties [Yang, 1999]. The colour of PVC products can be altered with pigments according to the desired application. It is supplied in powder form. The density of a rigid PVC sheet ranges from 1.3-1.45 g/cm$^3$ and that of flexible sheets ranges between 1.1 and 1.35 g/cm$^3$ [Chauffoureaux, 1979].

Additives that can be found in PVC include fillers, stabilisers, plasticisers, pigments and many more. Fillers can be added to the polymer to improve processing and mechanical properties, reduce costs and to add bulk to the plastic [Wiebking, 1998]. Fillers are mainly inexpensive inert materials that are generally inorganic and polar. The chemical composition of fillers has a great influence on polymer-filler compatibility and interaction [Wiebking, 1998]. The particle size, shape and distribution as well as surface chemistry of fillers differ and is responsible for its characteristic strength or weakness when used in polymers [Bryant, 2002]. The amount of filler added to a polymer depends on the physical requirements of the product.

Calcium carbonates are widely used as functional fillers in rubber and plastic because of their ability to improve impact strength, replace expensive plastic resin and act as a processing aid [Xanthos, 2005 and Wiebking, 1998]. Their optical properties are also important to their functionality as filler. The particle size of a filler is important in polymer processing, since it can affect the cohesiveness of the produced material [Wiebking, 1998].
Fly ash has similar chemical and physical properties as calcium carbonate, however some differences do exist [Schut, 1999]. Its characteristics are highly comparable to several commercial fillers [Huang, 2003]. The spherical nature of fly ash has been reported to add rigidity and compressive strength to plastic compounds and improve throughput but can lead to increased frail points on plastic formulations [Schut, 1999]. The varying particle size and colour of fly ash have been reported to be unfavourable characteristics of the fly ash as a filler [Bryant, 2002].

Fly ash is a cheaper filler in comparison to calcium carbonate due to its low density. The reported density of fly ash is approximately 2.22 g/cm$^3$ with that of calcium carbonate being 2.70 g/cm$^3$. This implies that a smaller amount of fly ash can be used in a polymer formulation to give the same physical properties as using a higher amount of calcium carbonate [Schut, 1999].

Fly ash and cenospheres have been studied as filler for different polymers and rubbers and the research in this field is growing exponentially. Yang et al. [1999] reported that an additive of 10% of untreated fly ash to PVC reduced the wear when compared to PVC without the additive. The effects of fly ash on polymers and rubbers have been found to improve when the fly ash samples used had undergone some kind of treatment. Yang et al. [2006] studied the surface modification of purified coal fly ash, with subsequent application in polypropylene and reported higher mechanical performance for the modified fly ash.

Deepthi et al [2010] reported that the addition of surface modified cenospheres to polyethylene increased the tensile strength values. He also mentioned that the spherical nature of the cenospheres impacted negatively on the values obtained for the elongation at break tests, and that the samples did not undergo sufficient elongation.

Li et al [1998] reported that fly ash added to post-consumer PET plastic waste did not only act as a filler but also as a heat conductor, decomposition inhibitor as well as a lubricating agent. Fly ash can be used in polymers to enhance more than one of its important functions.
8.2 Experimental

Different amounts of untreated and treated fly ash samples were tested as filler. Flexible PVC sheets were made with CaZn as a stabiliser and Di-Octyl phthalate as the plasticiser. Three different ratios of filler to resin namely, 30, 40, and 70 phr with 100 g of PVC powder, 3 g of stabiliser and 40 g of plasticiser per sample as indicated in Table 8.1.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Parts per hundred resin (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC S68</td>
<td>100</td>
</tr>
<tr>
<td>Fly ash (Treated or untreated)</td>
<td>30, 40, 70</td>
</tr>
<tr>
<td>Stabiliser (Ca/Zn stearate)</td>
<td>3.0</td>
</tr>
<tr>
<td>Plasticiser (Di Octyl phthalate)</td>
<td>40.0</td>
</tr>
</tbody>
</table>

Two CaCO$_3$ fillers, Kulubrite 2 and Kulucote 2 (2% stearic acid coated CaCO$_3$), namely were also tested as standard filler for comparison purposes. A filler to resin ratio of 30 phr was tested for the two CaCO$_3$ fillers. The dry samples, which include the PVC resin, the filler, and the stabiliser, were mixed together in a high speed mixer for 3 minutes before the liquid plasticiser was added to the mix. After adding the plasticiser, the contents were mixed together in the mixer for a further 5 minutes. The sample was collected and milled on a two roll bridge mill at 168 °C.

Tensile strength tests were done according to the method and provisions of ISO 527 part 1, on each of the samples, testing along the direction of milling as well as the transverse direction. The samples were cut with a die cutter, 5 specimens from each direction. The samples were then placed in the mechanical laboratory for 36 hours to condition at 23 °C and a humidity of 43%.

Tensile testing was done at a constant speed of 50 mm/min with a gauge distance of 50 mm according to ISO 527 for tensile strength and elongation analysis on flexible sheets. The relative densities of the different PVC composites were measured on a Micromeritics AccuPyc II, 1340 Gas Pycnometer instrument, at 25 °C under a pressure of 1 atm.
8.3 Results and discussion

8.3.1 Observations

The time for the formulation of 4.0 % SLS refluxed fly ash and PVC to form a homogenous band of material on the mill averaged at 6 minutes, while for CaCO$_3$ and PVC it averaged at 5 minutes for the 30 parts per resin formulation. The untreated fly ash and PVC formulation took longer to flux, averaging at approximately 8 minutes for 30 and 40 phr and 14 minutes for 70 phr respectively.

In comparison, the PVC filled with the SLS treated fly ash had a shorter flux time than the PVC filled with untreated fly ash. By increasing the filler loading to 70 phr a considerable increase in the mass of the composite is expected. This can explain the increased fluxing time of the 70 phr composite, resulting in a certain difficulty in processing.

8.3.2 Relative densities

The densities of the different formulations as given in Table 8.2 were found to be between 1.37 to 1.47 g/cm$^3$ indicating values typical of a rigid PVC [Chauffoureaux, 1979].

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Relative Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 phr kulubrite 2 (KB)</td>
<td>1.3982</td>
</tr>
<tr>
<td>30 phr kulucote 2 (KC)</td>
<td>1.3982</td>
</tr>
<tr>
<td>30 phr untreated fly ash</td>
<td>1.3763</td>
</tr>
<tr>
<td>30 phr treated fly ash</td>
<td>1.3745</td>
</tr>
<tr>
<td>40 phr untreated fly ash</td>
<td>1.3988</td>
</tr>
<tr>
<td>40 phr treated fly ash</td>
<td>1.4034</td>
</tr>
<tr>
<td>70 phr untreated fly ash</td>
<td>1.4691</td>
</tr>
<tr>
<td>70 phr treated fly ash</td>
<td>1.4772</td>
</tr>
</tbody>
</table>

Comparing the fillers at 30 phr, CaCO$_3$ was found to be heavier which is in agreement with previous results reported by Schut et al [1999]. With the same amount of filler different densities were observed, confirming the lower density of fly ash.
8.3.3 Mechanical Performance

The tensile strength and elongation at break, reported in Table 8.3, for the treated fly ash PVC formulation is marginally higher compared to that of the untreated fly ash PVC formulation. Elongation was also observed to be significantly elevated for the TFA formulation for the 30 and 40 phr, but not for the 70 phr as seen in Figure 8.1.

<table>
<thead>
<tr>
<th>Phr</th>
<th>FA Tensile Strength (MPa)</th>
<th>FA Elongation at break (%)</th>
<th>TFA Tensile Strength (MPa)</th>
<th>TFA Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>14.3±0.4</td>
<td>199.9±9.8</td>
<td>15.2±0.1</td>
<td>265.5±4.8</td>
</tr>
<tr>
<td>40</td>
<td>10.1±0.3</td>
<td>209.1±7.5</td>
<td>13.4±0.2</td>
<td>221.0±11.1</td>
</tr>
<tr>
<td>70</td>
<td>9.0±0.2</td>
<td>185.1±4.9</td>
<td>9.4±0.6</td>
<td>160.1±1.9</td>
</tr>
</tbody>
</table>

The values obtained for the elongation at break for the two CaCO$_3$ fillers were included (Table 8.4) to compare the elongation at break of the different fillers. Treated fly ash still showed a higher resistance to pulling force in comparison to the other fillers at 30 phr, with kulubrite 2 showing a slightly higher elongation at break between the two CaCO$_3$ fillers. The untreated fly ash was found to have the lowest resistance to pulling force.

<table>
<thead>
<tr>
<th>KB</th>
<th>KC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>15.6±0.9</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>238.5±21.3</td>
</tr>
</tbody>
</table>
Even though the tensile strength (Figure 8.2) of the formulation of the PVC containing TFA was found to be slightly higher than that containing the untreated FA; in comparison to the KB and KC filled PVC composites no significant difference was observed. Approximately the same tensile strength was obtained for the PVC containing treated fly ash and the two CaCO$_3$ fillers at a loading of 30 phr.
Similar results were obtained for the elongation at break tests performed on the resin formulations which were cut along the milling direction, compared to samples taken from the transverse direction. The elongation at break of the TFA and PVC formulation (Table 8.5 and Figure 8.3) was found to be significantly greater than that of the untreated FA. KB and KC elongation at break (Table 8.6 and Figure 8.3) was found to be slightly greater than that of the treated fly ash filler with KB being the highest.

### Table 8.5: Mechanical properties of untreated and treated fly ash filled PVC composites in transverse direction (TV)

<table>
<thead>
<tr>
<th>phr</th>
<th>FA</th>
<th>TFA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tensile Strength (MPa)</td>
<td>Elongation at break (to the nearest 5%)</td>
</tr>
<tr>
<td>30</td>
<td>9.8±0.4</td>
<td>147.6±24.2</td>
</tr>
<tr>
<td>40</td>
<td>9.3±0.5</td>
<td>143.2±18.9</td>
</tr>
<tr>
<td>70</td>
<td>8.7±0.3</td>
<td>111.2±13.2</td>
</tr>
</tbody>
</table>

The tensile strength of the samples taken in the transverse direction, Table 8.5 and 8.6 and Figure 8.4, decreased in comparison to those taken in the milling direction; however the same trend was seen for all the fillers. The tensile strengths obtained for the PVC resins containing SLS treated fly ash were higher than those containing untreated fly ash for all filler loadings. At a loading of 30 phr, the tensile strength of resins containing TFA and KC were equivalent.

### Table 8.6: Mechanical properties of KB and KC filled PVC composites in transverse direction (TV)

<table>
<thead>
<tr>
<th></th>
<th>KB</th>
<th>KC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>13.7±0.3</td>
<td>13.0±0.4</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>231.3±8.7</td>
<td>214.7±12.0</td>
</tr>
</tbody>
</table>
Figure 8.3: Comparison of the elongation at break of untreated fly ash (FA), treated fly ash (TFA), kulubrite 2 (KB) and kulucote 2 (KC) filled PVC composites in transverse direction.

Figure 8.4: Comparison of the tensile strength of untreated fly ash (FA), treated fly ash (TFA), kulubrite 2 (KB) and kulucote 2 (KC) filled PVC composites in transverse direction.

Alkan (1995) reported that the tensile strength of a resin is expected to decrease with increasing fly ash content, which was confirmed by the tensile strength observed for the 70 phr formulation in this study. The 30 phr filler loading was found to be the resin formulation that...
performed best compared to other filler loadings investigated in this study. It was observed to have a greater tensile strength and elongation at break in comparison to the other ratios. This indicates the ability of the formulation to withstand pressure and has shown increased durability.

The increased volume of fly ash particles in the resin formulation influences the elongation at break as well as the tensile strength. Figure 8.5 represents the SEM micrographs of the treated fly ash samples and PVC formulation for the different amounts of filler added. The micrographs show the volume of the fly ash particles in formulation and the breaking points which occur at the contact point of the PVC and fly ash.

The greater the volume of fly ash particles the greater the points of possible breaks hence the observed low values of elongation at break with increased amounts of filler. The spherical nature of the fly ash as seen in the micrographs can also influence the breaking patterns [Deepthi, 2010]. Since their stability prevents them from breaking, or disintegrating, the break point is observed at the point of contact between the spherical fly ash particles and the PVC resin.

![SEM micrographs of the fracture surface of untreated fly ash samples and PVC formulation for the different amounts of filler added](image)

**Figure 8.5:** SEM micrographs of the fracture surface of untreated fly ash samples and PVC formulation for the different amounts of filler added
The fly ash particles are seen to be mixed homogeneously with the PVC resin with a certain level of even distribution allowing for good interactions between the two materials, Figures 8.5.

![30 phr TFA and PVC formulation](image1.jpg)

![40 phr TFA and PVC formulation](image2.jpg)

![70 phr TFA and PVC formulation](image3.jpg)

Figure 8.6: SEM micrographs of the fracture surface of SLS treated fly ash samples and PVC formulation for the different amounts of filler added

Figure 8.7 indicates the fracture surface of the CaCO$_3$ filler and shows its irregular shape. The particles are spread throughout the formulation and the fracture points do not only occur at filler–resin interaction as seen with fly ash.

![Kulubrite 2](image4.jpg)

![Kulucote 2](image5.jpg)

Figure 8.7: SEM micrographs of the CaCO$_3$ and PVC formulation for 30 phr
8.4 Conclusion

The tensile strength of the SLS treated fly ash-PVC formulation was found to be greater than the formulation containing untreated fly ash and at a loading of 30 phr, the resin containing SLS treated fly ash showed maximum strength. The tensile strength of the PVC resin with treated fly ash, kulubrite 2 and kulucote 2 used as fillers are comparable at 30 phr, however the elongation at break of the composites containing the CaCO$_3$ fillers was found to be greater. Greater amounts of filler (FA or TFA) in the formulation resulted in a decrease in the tensile strength and decreased elongation at break.

Treatment of fly ash with SLS was found to be favourable, since an increase in tensile strength and elongation at break was observed for the TFA filled PVC, when compared to the PVC containing untreated fly ash at similar loadings. This can possibly be ascribed to the fact that the treated fly ash has better particle separation and can therefore have enhanced particle–particle interaction with the resin.

When considering only the strength and elongation tests, these results indicate that SLS treated fly ash can successfully replace CaCO$_3$ as filler in PVC when a low loading of filler is used. However, these tests are preliminary and further research work need to be done; this may include optimisation of the filler-PVC formulation. The fly ash containing a lower degree of surfactant coating may also be tested as possible filler. Due to the grey colour of the fly ash, the poor colour characteristics of the obtained fly ash-PVC resins also remain a concern.
8.5 References


CHAPTER 9

CONCLUSION AND RECOMMENDATIONS

9.1 Conclusion

This study, in the first place characterised some of the chemical, physical and surface properties of untreated South African fly ash using a number of analytical and physical techniques. Secondly, the surface properties of fly ash were modified using the surfactant sodium lauryl sulphate (SLS) under a range of different experimental conditions. Thirdly, the chemical and physical properties of the surfactant treated fly ash samples were compared to that of the untreated fly ash. Lastly, the validity of the experimental results was tested by performing a feasibility study to investigate if the SLS treatment of fly ash samples improved the workability of fly ash as filler in PVC.

A number of conclusions can be drawn from the results obtained from each technique used during the study namely:

- XRD analysis showed that 62% of the untreated fly ash sample used in this study consists of an amorphous glass phase with the main crystalline phases mullite and α-quartz. The chemical composition, as determined by XRF analysis, confirmed that the studied fly ash is a Class F fly ash with low CaO content. The introduction of aqueous surfactant solutions or additional electrolytes in the form of salts to the surfactant treatment solutions did not alter the phase or chemical composition of the ash. Although the phase and chemical composition of the SLS modified coal fly ash samples was not altered extensively, significant changes could be observed in its physical properties.

- The spherical morphology and small particle size of the fly ash may enhance its applicability as filler in polymers. The results obtained from SEM show significant agglomeration between the untreated fly ash particles. TEM analysis indicated that the untreated fly ash sample has a relatively smooth surface topography, with few agglomerates on its surface.
Compared to that of the untreated fly ash, the SEM micrographs show a change in the particle distribution observed on the SLS modified fly ash samples, implying better particle separation for the treated samples. The median particle size of the fly ash samples decreased upon treatment, confirming breakdown of agglomerates. Nath et al [2010a] also reported a reduction in particle-particle interaction upon surfactant treatment of Australian coal fly ash, but found an increase in the particle size of the size fraction below 25 microns. The author attributed this to the coating of surfactant on the surface of the fly ash. In this study, the occurrence of needle-like surfactant agglomerates on the surface of the SLS modified fly ash seen on the SEM images was confirmed by TEM analysis. An increase in the median particle size of the fly ash was however not observed. The morphology of the agglomerates on the untreated fly ash was distinctively different from those on the SLS modified fly ash and between samples treated under different conditions. The modified fly ash particles were not all covered with surfactant agglomerates to the same degree.

The introduction of a counter ion in the surfactant solution increased the aggregation of the surfactant onto the surface of the fly ash, which led to a decrease in the extent of agglomeration between fly ash particles.

The phases detected in the Raman and FTIR spectra for the untreated fly ash agrees well with the results obtained from XRD. Raman 2D mapping provided a good spatial representation of the distribution of the different phases in the samples. Interactions between fly ash particles and SLS could be deduced from the FTIR results, where a small shift in peak positions of the S-O stretch was observed. This may be indicative of electrostatic interactions rather than bonding interactions between SLS and the fly ash surface. The peaks of the C-H stretch region did not display a shift, pointing that the interaction between SLS and fly ash may take place through the sulphate anion. This implies that the hydrocarbon chain is aligned outwards from the fly ash kernel, which would explain the hydrophobic behaviour observed in the contact angle experiments. The needle-like shape of the agglomerates observed in the TEM images supports these observations.
• TGA-FTIR measurements of the untreated fly ash sample showed a very low weight loss up to 400 °C. The thermal stability of fly ash up to this temperature can be considered an added advantage when using it as filler in polymers, since general polymer processing temperatures are below this temperature, and low filler volatility is advantageous.

• The results obtained from TGA measurements showed a significant weight loss over the temperature range of 230 to 250 °C for the surfactant treated fly ash samples, and CH₂ and CO₂ could be identified as decomposition products in the gas phase FTIR data. The occurrence of CH₂ as a decomposition product can be ascribed to the presence of hydrocarbons originating from the SLS in the modified fly ash sample, while CO₂ points to the onset of oxidation of residual coal within the fly ash. These results confirm the FTIR results obtained for the treated fly ash samples.

• Contact angle measurements were performed to investigate changes upon wettability of the fly ash samples. The surfactant coating on the modified fly ash samples, as observed on the TEM, changes the surface of the fly ash from hydrophilic to hydrophobic, thus the inability of the water droplet to disperse on the surface.

• The use of modified fly ash as filler to PVC was found to be favourable, since an increase in tensile strength and elongation at break, in comparison to untreated fly ash filled PVC, was observed. Nath et al [2010b] reported an enhanced strength of approximately 33% for SLS-FA filled PVA when compared to FA filled PVA. This can possibly be ascribed to the fact that the treated fly ash has better particle separation and therefore enhanced particle–particle interaction within the resin. Changing the wettability of fly ash from hydrophilic to hydrophobic enhanced compatibility between the fly ash filler and PVC matrix.

• Results from the feasibility study proved that SLS treated fly ash can replace CaCO₃ in PVC at low filler loading. However the grey colour of fly ash is a disadvantage when compared to white CaCO₃.
9.2 Recommendations

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. The reactivity of the fly ash towards other types of surfactants will also be investigated, with the aim of enhancing interaction between the surfactant and polymer.

From the results obtained, it is evident that further investigations need to be performed in order to fully understand the interactions between SLS and the fly ash surface. The occurrence of agglomerates on the surface of the SLS modified fly ash was confirmed by TEM and SEM measurements, but its exact structure and composition is not known yet.

9.3 References