

Focke: Brief description of research 2009 - 2016

Chemical and polymer technology

My research focus is on chemical and polymer technology. In this broad field I have research activities in carbon technology, clay and polymer additive technology and pyrotechnics.

1. Carbon technology

The original objective of the IAM research in carbon technology was to investigate the synthesis and characterisation of nuclear-grade graphite from local South African raw materials. This was initiated in support of the now defunct Pebble-Bed reactor project. Since its demise, the focus of the larger IAM Carbon Group has shifted to graphite for energy applications. That includes solar thermal energy storage, where the high thermal conductivity of graphite is relevant. My own research considers graphite as a functional additive for polymers to improve fire resistance and electrical conductivity.

Synthesis & characterization of carbon precursor materials and modified graphite materials.

Various carbon and graphite precursor routes were evaluated and the materials characterised [1-4]. Compression moulded carbon/graphite composites were prepared and tested [5]. A novel process for graphite foam, was developed [6]. It is based on the exfoliation of expandable graphite in a pitch precursor. These low-cost foams feature reasonably high thermal conductivity.

Characterising the high-temperature oxidation of graphite. Knowledge of the oxidation behaviour of nuclear graphite was considered important for the simulation of possible accident scenarios in Pebble bed reactors. Meticulous use of high resolution electron microscopy and thermal analysis techniques revealed that the oxidation of graphite, even those of highest purity, is dominated by the effect of catalytic impurities [7]. Mathematical models were developed for the oxidation rate of graphite materials [7-10].

Improving the fire resistance, mechanical and antistatic properties of polymers with clays and graphite. In South Africa, polyolefin products are used in deep level mining applications. They pose a significant fire risk that must be mitigated through the use of non-toxic flame retardants. One way to impart fire resistance is to force the polymer degradation reactions towards char formation as this reduces the generation of flammable fuel.

Incorporation of graphite, specifically expandable and graphite nanoplatelets, significantly improves the antistatic properties of polyethylene [11] and the thermal conductivity of thermal energy storage materials [12]. There are also positive effects on the fire resistance of PVC [13] and polyethylene [14-19] especially when used in combination with intumescent flame retardants. Unfortunately graphite imparts a deep black colour to components. Therefore, vermiculite was considered as an alternative [20]. It also exfoliates explosively just like expandable graphite but this happens at temperatures above the degradation temperature of the polymers. However, we managed to reduce the exfoliation onset temperature [20, 21] and this resulted in vermiculite providing improved flame retardancy to selected polymers [20].

Incorporating graphite into polyethylene reduces its impact strength. Good impact strength can be retained using a double dumping technique to rotomould laminated products in which a thin outer layer, based on graphite filled EVA, covers the main body made from polyethylene. Such sheets also showed excellent fire resistance in cone calorimeter tests [22].

2. Clay and polymer additive technology

Thermal analysis techniques are used to study (a) the oxidation behaviour of materials targeting either the inhibition or enhancement of the rates of degradation or combustion; and (b) the release rates of migrating or volatile actives such as volatile corrosion inhibitors and insect repellents. The synthesis, purification and processing of clays, carbons, graphite is targeted towards additive applications in polymers. They are used to prepare and characterise polymers and polymer macro- & nanocomposites with improved properties. Of particular interest are improvements in thermo-oxidative stability, flame retardancy and controlled release of actives. Most of the research funding comes from industry and it is therefore obvious that there are market needs that the sponsors want to address.

Volatile corrosion inhibitors. Protective film packaging for metals subjected to atmospheric corrosion. In South Africa the largest application is the use of VCI's in polyethylene film used to wrap steel rolls. We have developed proprietary VCI's that are currently used for this application. A simple thermogravimetric technique was previously developed for the estimation of the air permeability (i.e. the product of the vapour pressure and the diffusion coefficient in air) of organic compounds [23, 24]. This knowledge is important for designing systems that rely on the release of vapours into air, e.g. volatile corrosion inhibitors and insect repellents. This TGA technique was used to gain an understanding of the evaporation mechanism of volatile corrosion inhibitors (VCI's) [25, 26] and to develop new proprietary commercial products.

Synthesis and chemical and/or physical modification of clays and other micro- or nano-sized particles. The objective is to add value to local and Mozambican clay deposits as well as anionic clays synthesized by local company. The target is to convert these synthetic & natural clays into effective polymer additives that improve physical properties. New methods for the purification and synthesis of organoclays were developed. These clays were developed for use as additives in order to modify oil- and polymer properties [20, 21, 27-32].

Polymer nanocomposites. The market need is to improve mechanical and other physical properties of polymers. Polymer nanocomposites with improved functional and mechanical properties were prepared and characterised [12, 33-38]. It turned out that layered double hydroxides provide a dual function to PVC simultaneously improving heat stability and fire retardancy [27, 39, 40]. Some nanoparticles acted as excellent nucleating agents facilitating rapid crystallization of selected polymers even at extremely high cooling rates [41, 42]. Organo-modification of clays with the matrix polymer itself proved feasible for polyamides and led to materials with significantly improved stiffness [37, 38, 43, 44].

Characterising and modulating the heat stability of PVC and the thermal- and UV degradation of polyolefins and biodiesel. The objectives was the stabilisation of polymers, carbon materials or biodiesel and against oxidative degradation mediated by heat or UV radiation. For quality control purposes, it is common to use either the isothermal oxidation induction times (OIT) or the dynamically evaluated oxidation onset temperatures (OOT) as measures of the oxidative stability of a polyethylene and polypropylene. It was found that these quantities are related as they correspond to similar level of antioxidant depletion [45]. Sunflower-derived biodiesel is particularly prone to oxidative degradation [46]. A new method for estimating the oxidative stability of biodiesel from Rancimat data was proposed [47]. Reduction of the visual impact of plastic litter from packaging and plastic shopping bags was targeted by enhancing the UV degradation rate of polyolefin films. Fatty acid intercalated transition metal layered double hydroxides and metal stearates were found to be effective photo-prodegradants [48, 49]. Use of such materials should not prevent recycling of such plastic waste: It also proved possible to re-stabilise polyethylene containing these oxo-prodegradants by adding suitable anti-oxidants [48].

Malaria vector control. The Institute of Sustainable Malaria Control at the University of Pretoria is a large multidisciplinary research effort. My Chemical and Polymer Technology research group forms part of the malaria vector control activity. Our research focus in this topic is informed by the research results generated by public health researchers and entomologists. Our objective is to use our skills in chemical and polymer technology to develop novel products for malaria vector control. The target is controlled release of actives such as insecticides and repellents from polymer matrices. New approaches for both indoor and outdoor protection against malaria transmission were developed [50-55]. A polypropylene bed net with betacyfluthrin as insecticide was able to withstand the large number

of washes prescribed by WHO specifications [54]. The trick was to use a crystalline insecticide that does not melt at wash temperatures and hence it is retained on the textile fibres.

Despite serious health concerns, indoor spraying of DDT is still practised in Southern Africa. The reason is the poor environmental stability of safer insecticides. Through a Bill & Melinda Gates Foundation grant, it was found that catalytic hydrolysis is the mainly cause [52]. It was found possible to stabilise WHO-approved pyrethroid insecticides by absorbing them on a low pH filler such as phospho-gypsum [50] or by co-intercalating them in clays [53]. In laboratory bioassay tests such materials outperformed DDT, even on cow dung-coated surfaces. Even better performance was achieved by incorporating the insecticides into a low-cost polyethylene wall lining [51]. Field trials and bioassays have shown that the efficacy of these linings is retained for several years [51]. This technology is being licenced to a commercial company for wider application.

For brief overviews of our malaria research see:

http://www.up.ac.za/media/shared/Legacy/sitefiles/file/44/1026/2163/8121/innovate8/4045physical_chemical_and_biological_strategies_to_combat_malariabymthokozisimsibandaetal.pdf

3. Pyrotechnics

The objective was to develop “green” pyrotechnic compositions for use as time delays and initiating compositions in chemical mine detonators. New “green” pyrotechnic formulations suitable for short-, medium- and long-time delay applications were developed [56-61]. The Mn-MnO₂ system [61] was patented as a “green” medium burning rate system. It is unique in that it features a metal reacting with its own “rust”! Three novel approaches to reduce the evolution of hydrogen gas by aqueous silicon dispersion were found [62-64]. A novel approach, to prepare a robust pyrotechnic formulation was found by combining a redox and an intermetallic reaction. This keeps the energy output at a plateau value over a relatively wide stoichiometric range [58]. A sophisticated numerical model for the prediction of burn rates of time delays was developed [65]. It makes it possible to optimise such systems. The chemical reaction kinetics of both slow and fast burning compositions were indirectly inferred from the temporal evolution of surface temperature on the outside of burning columns. Using copper antimonite with silicon as fuel gives particularly insensitive pyrotechnic formulations. A new way of synthesising this interesting oxidiser was developed [66]. Its unique crystal structure and unusual magnetic properties were studied [67].

For a brief overview of our activities in green pyrotechnic research

see: http://www.up.ac.za/media/shared/Legacy/sitefiles/file/44/1026/2163/8121/innovate8/119121towards_greener_pyrotechnicsbyprofwalterfockeetal.pdf

References

1. Makgato, M.H., et al., *Alkali-assisted coal extraction with polar aprotic solvents*. Fuel Processing Technology, 2009. **90**(4): p. 591-598.
2. Papole, G., W.W. Focke, and N. Manyala, *Characterization of medium-temperature Sasol-Lurgi gasifier coal tar pitch*. Fuel, 2012. **98**: p. 243-248.
3. Ramjee, S., B. Rand, and W.W. Focke, *Low shear rheological behaviour of two-phase mesophase pitch*. Carbon, 2015. **82**(C): p. 368-380.
4. Hlatshwayo, S.R., et al., *Rheological behavior and thermal properties of pitch/poly(vinyl chloride) blends*. Carbon, 2013. **51**(1): p. 64-71.
5. Magampa, P.P., N. Manyala, and W.W. Focke, *Properties of graphite composites based on natural and synthetic graphite powders and a phenolic novolac binder*. Journal of Nuclear Materials, 2013. **436**(1-3): p. 76-83.

6. Focke, W.W., et al., *Graphite foam from pitch and expandable graphite*. Carbon, 2014. **73**: p. 41-50.
7. Badenhorst, H. and W.W. Focke, *Geometric effects control isothermal oxidation of graphite flakes*. Journal of Thermal Analysis and Calorimetry, 2012. **108**(3): p. 1141-1150.
8. Badenhorst, H., B. Rand, and W.W. Focke, *Modelling of natural graphite oxidation using thermal analysis techniques*. Journal of Thermal Analysis and Calorimetry, 2010. **99**(1): p. 211-228.
9. Badenhorst, H. and W. Focke, *Comparative analysis of graphite oxidation behaviour based on microstructure*. Journal of Nuclear Materials, 2013. **442**(1–3): p. 75-82.
10. Badenhorst, H., B. Rand, and W. Focke, *A generalized solid state kinetic expression for reaction interface-controlled reactivity*. Thermochemica Acta, 2013. **562**: p. 1-10.
11. Mhike, W.F., W.W., *Surface resistivity and mechanical properties of rotationally molded polyethylene/graphite composites*. Journal of Vinyl and Additive Technology, 2013.
12. Mhike, W., et al., *Thermally conductive phase-change materials for energy storage based on low-density polyethylene, soft Fischer-Tropsch wax and graphite*. Thermochemica Acta, 2012. **527**: p. 75-82.
13. Focke, W.W., et al., *Flexible PVC flame retarded with expandable graphite*. Polymer Degradation and Stability, 2014. **100**(1): p. 63-69.
14. Mhike, W., et al., *Flame retarding effect of graphite in rotationally molded polyethylene/graphite composites*. Journal of Applied Polymer Science, 2015. **132**(7).
15. Kruger, H.J., et al., *Thermal properties of polyethylene flame retarded with expandable graphite and intumescent fire retardant additives*. Fire and Materials, 2016.
16. Focke, W.W., et al., *Polyethylene flame retarded with expandable graphite and a novel intumescent additive*. Journal of Applied Polymer Science, 2014: p. n/a-n/a.
17. Kruger, H.J.F., W.W.; Mhike, W.; Taute, A.; Ofosu, O., *Cone calorimeter study of polyethylene flame retarded with expandable graphite and intumescent fire retardant additives*. 2014.
18. Focke, W.W.M., W.; Kruger, H. J.; Van Schalkwyk, R.; Lombaard, D.; Badenhorst, H. , *Thermal Analysis of Commercial Expandable Graphite Flame Retardants*. 2014.
19. Focke, W.W., et al., *Characterization of commercial expandable graphite fire retardants*. Thermochemica Acta, 2014. **584**: p. 8-16.
20. Muiambo, H.F., et al., *Thermal properties of sodium-exchanged palabora vermiculite*. Applied Clay Science, 2010. **50**(1): p. 51-57.
21. Muiambo, H.F., et al., *Characterization of urea-modified Palabora vermiculite*. Applied Clay Science, 2015. **105–106**: p. 14-20.
22. Mhike, W., et al., *Rotomoulded antistatic and flame retarded graphite nanocomposites*. 2016.
23. Pieterse, N., et al., *Estimating the gas permeability of commercial volatile corrosion inhibitors at elevated temperatures with thermo-gravimetry*. Corrosion Science, 2006. **48**(8): p. 1986-1995.
24. Pieterse, N. and W.W. Focke, *Diffusion-controlled evaporation through a stagnant gas: Estimating low vapour pressures from thermogravimetric data*. Thermochemica Acta, 2003. **406**(1-2): p. 191-198.
25. Focke, W.W., N.S. Nhlapo, and E. Vuorinen, *Thermal analysis and FTIR studies of volatile corrosion inhibitor model systems*. Corrosion Science, 2013.
26. Nhlapo, N.S., W.W. Focke, and E. Vuorinen, *TGA-FTIR study of the vapors released by triethylamine-acetic acid mixtures*. Thermochemica Acta, 2012. **546**: p. 113-119.
27. Focke, W.W., et al., *The influence of stearic acid coating on the properties of magnesium hydroxide, hydromagnesite, and hydrotalcite powders*. Journal of Materials Science, 2009. **44**(22): p. 6100-6109.
28. Focke, W.W., et al., *Thermal properties of lauric- and stearic acid intercalated layered double hydroxides*. Molecular Crystals and Liquid Crystals, 2010. **521**: p. 168-178.

29. Massinga, P.H., et al., *Alkyl ammonium intercalation of Mozambican bentonite*. Applied Clay Science, 2010. **49**(3): p. 142-148.
30. Massinga, P.H. and W.W. Focke, *Intercalating Cationic Surfactants in Koppies Bentonite*. Molecular Crystals and Liquid Crystals, 2012. **555**(1): p. 85-93.
31. Moyo, L., et al., *Layered double hydroxide intercalated with sodium dodecyl sulfate*. Molecular Crystals and Liquid Crystals, 2012. **555**: p. 51-64.
32. Atanasova, M.T., et al., *Characterization of rectorite from the Beatrix Gold Mine in South Africa*. Applied Clay Science, 2016. **126**: p. 7-16.
33. Joseph, S. and W.W. Focke, *Poly(ethylene-vinyl co-vinyl acetate)/clay nanocomposites: Mechanical, morphology, and thermal behavior*. Polymer Composites, 2011. **32**(2): p. 252-258.
34. Manhique, A., et al., *Layered double hydroxides as nano additives in poly(ϵ -caprolactone)*. Molecular Crystals and Liquid Crystals, 2012. **556**: p. 114-123.
35. Moyo, L., et al., *Properties of layered double hydroxide micro- and nanocomposites*. Materials Research Bulletin, 2013. **48**(3): p. 1218-1227.
36. Massinga, P.H., et al., *EVA nanocomposites based on South African Koppies clay*. Journal of Vinyl and Additive Technology, 2014. **20**(3): p. 143-151.
37. MacHeca, A.D., et al., *Stiffening mechanisms in vermiculite-amorphous polyamide bio-nanocomposites*. European Polymer Journal, 2016. **74**: p. 51-63.
38. Macheca, A., D. Gnanasekaran, and W.W. Focke, *Surfactant-free dimer fatty acid polyamide/montmorillonite bio-nanocomposites*. Colloid and Polymer Science, 2013: p. 1-8.
39. Molefe, D.M., et al., *The effect of magnesium hydroxide, hydromagnesite and layered double hydroxide on the heat stability and fire performance of plasticized poly(vinyl chloride)*. Journal of Fire Sciences, 2015. **33**(6): p. 493-510.
40. Labuschagne, F.J.W.J., et al., *Heat stabilising flexible PVC with layered double hydroxide derivatives*. Polymer Degradation and Stability, 2015. **113**: p. 46-54.
41. Mollova, A., et al., *Crystallization of nanocomposites of an isotactic random butene-1/ethylene copolymer and layered double hydroxide*. Polymer Bulletin, 2013: p. 1-14.
42. Kolesov, I., et al., *Crystallization of a polyamide 11/organo-modified montmorillonite nanocomposite at rapid cooling*. Colloid and Polymer Science, 2013: p. 1-9.
43. Focke, W.W., et al. *Stiffening mechanisms in amorphous polyamide bio-nanocomposites*. in *AIP Conference Proceedings*. 2016.
44. Jariyavidyanont, K., W. Focke, and R. Androsch, *Crystallization kinetics of polyamide 11 in the presence of sepiolite and montmorillonite nanofillers*. Colloid and Polymer Science, 2016. **294**(7): p. 1143-1151.
45. Focke, W.W. and I. Van Der Westhuizen, *Oxidation induction time and oxidation onset temperature of polyethylene in air: Testing Gimzewski's postulate*. Journal of Thermal Analysis and Calorimetry, 2010. **99**(1): p. 285-293.
46. Focke, W.W., et al., *The effect of synthetic antioxidants on the oxidative stability of biodiesel*. Fuel, 2012. **94**: p. 227-233.
47. Focke, W.W., I.v.d. Westhuizen, and X. Oosthuysen, *Biodiesel oxidative stability from Rancimat data*. Thermochimica Acta, 2016. **633**: p. 116-121.
48. Focke, W.W., R.P. Mashele, and N.S. Nhlapo, *Stabilization of low-density polyethylene films containing metal stearates as photodegradants*. Journal of Vinyl and Additive Technology, 2011. **17**(1): p. 21-27.
49. Magagula, B., N. Nhlapo, and W.W. Focke, *Mn2Al-LDH- and Co2Al-LDH-stearate as photodegradants for LDPE film*. Polymer Degradation and Stability, 2009. **94**(6): p. 947-954.
50. Sibanda, M., et al., *The development of slow-release filaments to control malaria*, in *Innovate*. 2016, Graduate School of Technology Management, University of Pretoria: Pretoria, South Africa. p. 94-95.

51. Kruger, T., et al., *Acceptability and effectiveness of a monofilament, polyethylene insecticide-treated wall lining for malaria control after six months in dwellings in Vhembe District, Limpopo Province, South Africa*. Malaria Journal, 2015. **14**(1).
52. Sibanda, M.M., et al., *Degradation of insecticides used for indoor spraying in malaria control and possible solutions*. Malaria Journal, 2011. **10**.
53. Merckel, R.D., et al., *Co-Intercalation of Insecticides with Hexadecyltrimethylammonium Chloride in Mozambican Bentonite*. Molecular Crystals and Liquid Crystals, 2012. **555**(1): p. 76-84.
54. Focke, W.W. and W. Van Preen, *Polypropylene-based long-life insecticide-treated mosquito netting*. Journal of Polymer Engineering, 2011. **31**(6-7): p. 521-529.
55. Akhtar, M.U. and W.W. Focke, *Trapping citronellal in a microporous polyethylene matrix*. Thermochimica Acta, 2015. **613**: p. 61-65.
56. Tichapondwa, S.M., et al., *A Comparative Study of Si-BaSO₄ and Si-CaSO₄ Pyrotechnic Time-Delay Compositions*. Journal of Energetic Materials, 2016. **34**(3): p. 342-356.
57. Tichapondwa, S.M., et al., *The Effect of Additives on the Burning Rate of Silicon-Calcium Sulfate Pyrotechnic Delay Compositions*. Propellants, Explosives, Pyrotechnics, 2016: p. n/a-n/a.
58. Montgomery, Y.C., et al., *Mn+Sb₂O₃ Thermite/Intermetallic Delay Compositions*. Propellants, Explosives, Pyrotechnics, 2016: p. n/a-n/a.
59. Tichapondwa, S.M., et al., *Calcium Sulfate as a Possible Oxidant in "Green" Silicon-based Pyrotechnic Time Delay Compositions*. Propellants, Explosives, Pyrotechnics, 2015. **40**(4): p. 518-525.
60. Ilunga, K., et al., *The effect of Si-Bi₂O₃ on the ignition of the Al-CuO thermite*. Powder Technology, 2011. **205**(1-3): p. 97-102.
61. Swanepoel, D., et al., *Manganese as fuel in slow-burning pyrotechnic time delay compositions*. Propellants, Explosives, Pyrotechnics, 2010. **35**(2): p. 105-113.
62. Tichapondwa, S.M., et al., *Suppressing hydrogen evolution by aqueous silicon powder dispersions by controlled silicon surface oxidation*. Propellants, Explosives, Pyrotechnics, 2013. **38**(1): p. 48-55.
63. Tichapondwa, S.M., et al., *Suppressing H₂ evolution by silicon powder dispersions*. Journal of Energetic Materials, 2011. **29**(4): p. 326-343.
64. Tichapondwa, S.M., et al., *SUPPRESSING HYDROGEN EVOLUTION BY AQUEOUS SILICON POWDER DISPERSIONS THROUGH THE INTRODUCTION OF AN ADDITIONAL CATHODIC REACTION*. Chemical Engineering Communications, 2014. **201**(4): p. 501-515.
65. Montgomery, Y.C., W.W. Focke, and C. Kelly, *Measurement and modelling of pyrotechnic time delay burn rates: Method and model development*. Submitted for consideration as a publication in Propellants, Explosives, Pyrotechnics, 2017.
66. Focke, W.W., et al., *Facile synthesis of copper antimonite*. Chemical Engineering Communications, 2014. **201**(2): p. 153-159.
67. Atanasova, M.T., et al., *Crystal structure and magnetic properties of CuSb₂O₄*. Journal of Materials Science, 2014. **49**(9): p. 3497-3510.