28th October 2015 Monash University
Welcome to the 5th Annual Monash University Chemical Engineering Conference!
This conference builds upon the program introduced by the Chemical Engineering postgraduate association (CEPA) on 28th (Wednesday), Oct 2015. It provides researchers with an avenue to gain insight into the exciting research work undertaken in the Department of Chemical Engineering.

There are four main technical sessions within the conference and these reflect the research strengths of the department:

- Energy, Fuels, Biorefining & Sustainable Processing
- Biotechnology, Food & Pharmaceutical Technology
- Functional Nanomaterials
- Surface and Colloidal Science, and Molecular Rheology

The conference continues to provide a platform for researchers to showcase their research accomplishments. Additionally, some postgraduate students choose to complete their candidature milestones, either mid-candidature review or pre-submission seminar, during the conference.

On behalf of the Chemical Engineering Postgraduate Association (CEPA), we would like to thank you for attending the conference.

Sincerely,

CEPA Committee
## ORAL PRESENTATION

### SESSION A – Lecture Theatre E7, Building 72

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<td>09:30</td>
<td><strong>Energy, Fuels, Biorefining and Sustainable Processing</strong></td>
<td><strong>Chair: Craig Osborne</strong></td>
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<td></td>
<td>Use of beneficiated Victorian brown coal for blended combustion in PCI blast furnaces</td>
<td>Anthony De Girolamo</td>
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<td>09:55</td>
<td>Xanes iron k-edge speciation of heat transfer tube corrosion upon Victorian brown coal oxy-fuel combustion</td>
<td>Iman Ja’Baz</td>
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<td>10:20</td>
<td>Entrained flow pyrolysis and gasification of Victorian brown coal</td>
<td>Tao Xu</td>
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<td>10:45</td>
<td>Process simulation and exergy analysis for brown coal pyrolysis and gasification</td>
<td>Bai-Qian Dai</td>
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<td>11:40</td>
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<td>Yield and quality of bio-oil produced from catalytic pyrolysis of microalgae using Ni/ZSM-5 catalysts</td>
<td>Nur Hidayah Zainan</td>
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<td>12:05</td>
<td>Microwave pre-treatment of lignocellulosic biomass</td>
<td>Negin Amini</td>
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<td>Cellulose aerogel with tuneable pore structure for oil/water separation</td>
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<td>12:55</td>
<td>Lunch and poster presentation</td>
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<td>14:20</td>
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<td><strong>Chair: Huadong Peng</strong></td>
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<td>Production of agglomerates via 3D printing technology for granule breakage test</td>
<td>Ruihuan Ge</td>
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<td>14:45</td>
<td>Optimisation of detergent granulation processes to achieve rapid end-user dissolution and reduce drying time</td>
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<td>Understanding pharmaceutical dry powder blending – iron oxide tracer behaviour and different excipient powders</td>
<td>Kahlil Desai</td>
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<td>09:30</td>
<td>Functional nanomaterials</td>
<td>Chair: Kahlil Desai, Polysaccharide-based nanoparticle interactions with the immune system</td>
<td>Lecture Theatre E7, Building 72</td>
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<td>09:30</td>
<td><strong>Chair</strong>: Liam Powles</td>
<td>Polysaccharide-based nanoparticle interactions with the immune system</td>
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<td>09:55</td>
<td>Preparation and characterization of silica nanoparticle-cellulose</td>
<td>Chair: Liam Powles, Preparation and characterization of silica nanoparticle-cellulose nanofibre composites</td>
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<td>10:20</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt; branched rods photocatalytic membrane</td>
<td>Chair: Liam Powles, Preparation and characterization of silica nanoparticle-cellulose nanofibre composites</td>
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<td>10:45</td>
<td>Light and perspiration stability of triazinylstibene fluorescent</td>
<td>Chair: Liam Powles, Preparation and characterization of silica nanoparticle-cellulose nanofibre composites</td>
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<td>11:10</td>
<td>Morning tea</td>
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<tr>
<td>11:40</td>
<td>Chair: Liam Powles</td>
<td>Modification of an asymmetric porous polymer for high gas performance zif-8 membrane</td>
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<td>12:05</td>
<td>Copper nanowires as conductive ink for low cost draw-on electronics</td>
<td>Chair: Liam Powles, Preparation and characterization of silica nanoparticle-cellulose nanofibre composites</td>
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<tr>
<td>12:30</td>
<td>Rubber band-like wearable wireless biomedical sensors based on ionic</td>
<td>Chair: Liam Powles, Preparation and characterization of silica nanoparticle-cellulose nanofibre composites</td>
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<td>12:55</td>
<td>Post-synthetic Ti Exchanged UiO-66; enhancing the performance and</td>
<td>Chair: Liam Powles, Preparation and characterization of silica nanoparticle-cellulose nanofibre composites</td>
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<td>13:00</td>
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<td>13:20</td>
<td>Surface, Colloidal Science, and Molecular Rheology</td>
<td>Chair: Pradeep GC, Engineering the colloidal structure of nanocellulose fibres using polymers to control filtration and sheet properties</td>
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<td>14:20</td>
<td><strong>Chair</strong>: Pradeep GC</td>
<td>Engineering the colloidal structure of nanocellulose fibres using polymers to control filtration and sheet properties</td>
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<td>14:45</td>
<td>Coil-Stretch Hysteresis of Polymer Solutions at Finite Concentrations</td>
<td>Chair: Pradeep GC, Engineering the colloidal structure of nanocellulose fibres using polymers to control filtration and sheet properties</td>
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<td>15:10</td>
<td>Plasmonic nanoparticle synthesis, functionalization and sensing</td>
<td>Chair: Pradeep GC, Engineering the colloidal structure of nanocellulose fibres using polymers to control filtration and sheet properties</td>
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<td>Chair: Pradeep GC, Engineering the colloidal structure of nanocellulose fibres using polymers to control filtration and sheet properties</td>
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# Pre-submission Seminar
POSTER PRESENTATION

Size segregation of particles during filling a Paul-Wurth hopper
Tengfang Zhang

Biocompatible gold nanorods: synthesis and surface-modification
Kang Liu

Post-synthetic Ti exchanged UIO-66; enhancing the performance and industrial relevance of unsupported metal organic framework mixed matrix membranes
Stefan J. D. Smith
PHD IN CHEMICAL ENGINEERING
– HOW TO BE SUCCESSFUL DURING AND AFTER YOUR DEGREE?
Akshat Tanksale

Abstract
The decision to pursue a PhD degree can be a transformational one. What happens in the four years of the PhD program can have a huge impact on the career progression. Therefore making the most out of these years is essential, especially in a slow job market as experienced in the recent years. There are several pitfalls (sometimes chasms) that must be overcome during the course of the candidature. These hurdles are often not related to the topic of the research and are experienced by majority of the students. Staying motivated through these hurdles can often be challenging. Self-sabotaging or self-handicapping behaviour is often to blame for failure to overcome these hurdles or for significant delays in doing so. This presentation will cover topics that might help in improving productivity and effectivity (and not just efficiency). However, PhD is a not the endgame. PhD is only the start of a professional career. This presentation will review the recent trend in postgraduate destinations in Australia with the view to demonstrate employability and mobility of the PhD graduates. How does one prepare for the jobs outside of the obvious research and development work that PhD prepares the graduates for? What characteristics do the recent graduates have in common, which make them successful early in their career, irrespective of the sector in which they are working? These issues will be discussed, along with ideas for value adding to the PhD degree.

Biography
Dr Tanksale has a PhD (Chemical Engineering) from UQ (2008); a Master of Engineering (Chemical) from UQ (2004) and completed his Bachelor of Engineering (Chemical) at NIT, Raipur, India (2001). Dr Tanksale is an emerging leader in the field of catalysis and green chemistry. Application of his research is necessary to reduce human dependence on petroleum as a resource for fuels, chemicals and plastics production. He believes that innovating new processes and designing novel heterogeneous catalysts at the nanoscale is the key for developing alternative fuels and chemicals. His research is focused on developing catalysts and processes for converting lignocellulosic biomass into liquid fuels, hydrogen and value added chemicals. His research involves a multi-disciplinary approach which spans across materials science and engineering, including nanomaterials, physical chemistry and chemical engineering principles. In addition to his research leadership, Dr Tanksale is the Director of Graduate Research at the Department of Chemical Engineering, Monash University. In this role, he provides administrative support to the PhD candidates, chairs candidature milestone seminars and provides strategic advice to the department on the continuing implementation of best practices in graduate research and research training.
USE OF BENEFICIATED VICTORIAN BROWN COAL FOR BLENDED COMBUSTION IN PCI BLAST FURNACES

Anthony De Girolamo¹, Alex Grufas¹, Ilia Lyamin¹, Iori Nishio², Yoshihiko Ninomiya² and Lian Zhang¹

¹Department of Chemical Engineering, Monash University VIC 3800, Australia
²Department of Applied Chemistry, Chubu University, Aichi 387-8501, Japan

Extended Abstract

Introduction

One of the promising applications for Victorian brown coal (VBC) is as a substitute for bituminous coals used in pulverised coal injection (PCI) in a blast furnace. This may be achieved as a blend or as a complete replacement.

A previous study confirmed the viability of a complete replacement of commercial PCI coal with two chars derived from Yallourn brown coal [1]. The brown coal char replacement shows both beneficial and detrimental effects on performance. Yallourn char has a lower cost compared to PCI coal and contains a higher calorific value, meaning it can replace a greater portion of coke. On the other hand, Yallourn char has a higher ignition temperature due to the lower volatile content as well as having lower char reactivity. Char can be blended with the normal PCI coal to balance these characteristics, however it is not easily foreseeable how the created blend will behave due to possible synergistic interactions between different coals or chars [2].

In this study, the performance (properties and reactivity) and interaction of different mixtures of Yallourn char and commercial PCI coal will be analysed to determine an optimum ratio of blending. Techniques used include thermogravimetric analysis, ignition measured in a flat-flame burner, drop tube furnace experiments and CFD modelling.

Materials and Experimental

Yallourn char for this study is obtained by pyrolysis of raw wet Yallourn brown coal in a pilot scale shaft furnace. As in the previous study [2], two types of Yallourn char were produced under different conditions. These will be referred to as Yallourn char 1 (YC-1) and Yallourn char 2 (YC-2). The most common size fraction was taken from each of these (1-4 mm), ground to a size of <106 microns and mixed with a commercial PCI coal at four different blending ratios from 20% (mass fraction) to 80% char with the remaining PCI coal. The proximate analysis of both fuels is shown in Table 1.
Table 1: Proximate analysis of fuels

<table>
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<tr>
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<th>YC-1</th>
<th>YC-2</th>
<th>PCI coal</th>
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<tbody>
<tr>
<td>Moisture % ar</td>
<td>10.2</td>
<td>1.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Ash % db</td>
<td>6.7</td>
<td>5.2</td>
<td>8.7</td>
</tr>
<tr>
<td>Volatile matter % db</td>
<td>5.8</td>
<td>4.5</td>
<td>20.7</td>
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<tr>
<td>Fixed carbon % db</td>
<td>77.3</td>
<td>90.3</td>
<td>70.6</td>
</tr>
<tr>
<td>Lower heating value (MJ/kg)</td>
<td>27.2</td>
<td>32.3</td>
<td>30.5</td>
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Thermogravimetric analysis (TGA) was used to determine the ignition behaviour of the blends, the intrinsic reactivity kinetic parameters for pure fuels the burnout (percentage removal of carbon and other combustibles) of the unburned char samples collected after drop tube furnace experiments. Ignition tests were also carried out in a flat flame burner (FFB). The FFB was operated at atmospheric pressure with a measured flame temperature of 1062°C before addition of coal/char. Oxygen fraction was fixed at 0.21 and O₂/C ratio was fixed at 2.5.

A 2 m high drop tube furnace (DTF) was used to combust the coal and char sample and a gas analyser recorded the combustion gases exiting the furnace. The sample enters the drop tube furnace with a low volume primary gas, while a secondary gas is preheated and mixes with the coal or char at the injection point. Such a unique pre-heating system for the gas can resemble the blast furnace condition where coal is injected into a hot air stream. Temperatures 800, 900 and 1000°C were tested at O₂/C ratios ranging from 0.7 to 1.6.

Results and Discussions

Ignition temperature generally increases with increasing Yallourn char content. This is due to the lower VM %. However, the ignition temperature of blends increases non-linearly with reduced volatile matter content in the coals. Thus, the ignition temperature of the blends is lower than the weighted average of each respective coal and is not additive, indicating synergistic behaviour. At low blend ratios, YC-1 blends shows decreased or similar ignition temperature to that of the PCI coal, while YC-2 shows a low rate of increase in ignition temperature up to a 40% blend with ignition temperature increasing more sharply at higher blend ratios.

Experiments in the flat flame burner show an agreement with the ignition prediction by TGA. Figure 1 shows that ignition time may be lowered or be unaffected by blending at low ratios. As expected YC-2 blends shows a higher ignition delay than for YC-1 blends.
Figure 1 Ignition time for char blends as measured in the flat flame burner.

In the DTF at 1000°C, PCI shows higher burnout and faster burnout rate at lower O/C ratios (below 1.0) for YC-2, however is closely followed by 40-60% blends (with burnout amounts seen above 85% and 90% at these ratios), while for YC-1 burnout is maximized for the 80% blend. As the O₂/C ratio increases above 1.0, 40-60% YC-2 blends show best burnout performance (faster rate and higher values).

**Conclusions**

There is strong synergetic behaviour for the coal-char blend combustion. The ignition temperature increased non-linearly and was lower than the expected weighted averages. Burnout for the blends in the drop tube was maximized for a low blend ratio at low O₂/C ratios but for blends of similar Yallourn char and PCI coal contents at higher O₂/C ratios.

**Acknowledgements**

This work is supported by Coal Energy Australia (CEA), Brown Coal Innovation Australia (BCIA) and the Joint Partnership program between Australian Academy of Technological Science and Engineering, and Japan Society for the Promotion of Science (JSPS).

**References**


**Biography**

Anthony De Girolamo is a PhD candidate under supervision of Dr Lian Zhang. His research is focusing on development of a replacement for PCI coal by beneficiation of brown coal.
**XANES Iron K-Edge Speciation of Heat Transfer Tube Corrosion upon Victorian Brown Coal Oxy-Fuel Combustion**

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¹Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

²Department of Applied Chemistry, Chubu University, 1200 Matsumoto-Chō, Kasugai, Aichi, Japan

**Extended Abstract**

**Introduction**

All over the world, coal is the most abundant fossil fuel [1]. Based on the Key World Energy Statistics 2006 the recoverable reserves of coal are estimated approximately 120 billion tons [2]. Energy demand in the worldwide is forecast to increase about 40% by 2030. However, the electricity generated by coal is predicted to decline by 2040 [3]. The amount of coal consumed through the combustion process in power plants resulting in CO₂ emissions which contributes to global warming [4]. In order to reduce the CO₂ produced from coal-fired power plants, a variety of technologies for carbon capture and storage (CCS) have being developed in the world [5]. Oxy-fuel combustion is an attractive technology for curtailing greenhouse gas emissions from coal combustion [6]. In comparison to air-firing mode, oxy-fuel mode is able to deliver a flue gas mainly consisting of CO₂ and H₂O [7]. However, the impure components such as SO₂/SO₃ and HCl in the oxy-fuel flue gas are increased due to the flue gas recirculation, therefore, the tube corrosion in the heat-exchanger zone is supposedly altered [8, 9].

In this work, we presented the results for the influences of oxy-fuel combustion on the tube corrosion during Victorian brown coal combustion. Apart from two Victorian brown coal fly ashes (i.e. Hazelwood and Yallourn fly ash), three extra lignite fly ash samples were tested. A total of six different tube materials were tested as well. For each test, a tube was mounted in a fly ash sample, which was subsequently immersed in a typical oxy-firing flue gas environment for 50 hours. The temperature was maintained at 650°C throughout the test, as this temperature has been found being the worse temperature for tube corrosion in the super-heater zone in a boiler [10]. With regard to the tubes after test, each tube was quickly mounted and solidified into epoxy resin to avoid the surface oxidation in the ambient air. The cross-section was further polished and subjected to a variety of characterisation, optical microscopy (OM) to quantify the corrosion depth, scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX) detector to reveal the microstructure of corroded layer and the concentration profile of a variety of
elements of interest, and synchrotron X-ray absorption near edge spectroscopy (XANES) to quantify the speciation of iron (Fe) along the tube cross-section.

**Materials and Experimental**

A horizontal test furnace was used for tube corrosion test. The temperature was fixed to mimic post-combustion flue gas temperature with a range of 500-800°C, which is similar with the conditions near super-heater and re-heater in an industrial furnace. For each run, the ash sample was placed on the square specimen (tube plate) to mimic the ash deposition on a real steam tube surface. The tube specimen was then loaded on a quartz-made sample holder and pushed to the middle zone in the furnace, as shown in panel (a). The flue gas Compositions used are shown in Table 1 to mimic the typical air-firing and oxy-firing conditions. The gas flow rate is 300 mL/min. The furnace was kept in 650°C. Six tube materials were tested, including SS400, SUS304, SUS347, T23, T91, 12Cr1MoVG. Furthermore, the elemental compositions of five fly ash samples used are, including two Xinjiang ash (sub-bituminous coal, XJ and XJ_C), Hazelwood fly ash (HW), modified Hazelwood ash (HW_NaK) for the raw Hazelwood fly ash mixed with Na₂SO₄ (10 wt%) and K₂SO₄ (10 wt%), and Yallourn fly ash (YL). The concentration of Na₂SO₄ decreases in a sequence of HW < XJC < YL < XJ < HW_NaK.

**Results and Discussions**

The structures for the corroded tubes upon the interaction with Hazelwood fly ash in oxy-firing mode are illustrated in Figure.1. Clearly, all the tubes have been corroded significantly under the oxy-fuel case. Statistical analysis was conducted to quantify the thickness of the corrosion interface for each tube under the oxy-fuel mode. The results are depicted in Figure.2. Irrespective of fly ash type, the Cr content in tube material is in reverse proportion to the growth rate. That is, the SUS347 tube having the highest Cr content showed the least corrosion rate which is consistent to the literature finding [8]. For the tube T23 alloyed steel with the lowest Cr content, it was found to have the highest oxide thickness that is consistent with the literature [7]. The effect of fly ash type is marginal, given the fact that the experimental error is relatively large. In addition, the growth rate 0.2-1µm/h found here is also broadly consistent with the literature report on the tested alloy tubes with the similar Cr contents[11]
Conclusions
The following conclusions can be drawn from this work. Corrosion rate is around 0.2-1.0 \( \mu \text{m/hr} \) for tubes exposure to Hazelwood fly ash under oxy-fuel mode, decreasing with the increase on the content of Cr in tube, except T23. Penetration of oxygen is the main cause for tube corrosion in air-firing mode; whereas the penetration of both sulphur and oxygen corroded tube in the oxy-firing mode. EXANES analysis indicates that, hematite (Fe_2O_3) siderite (FeCO_3) and augite (NaFeO_2) are the major Fe-bearing species on the corroded tube surface.

Acknowledgements
The authors are grateful to BCIA and ANLEC who have supported this work. Appreciation is also extended to beamline scientists, in NSRRC of Taiwan for the XANES operation support.
References


Biography

Mrs. Iman Jabaz is a PhD student in the first year, who is working on the oxy-fuel combustion of Victorian brown coal.
Entrained flow pyrolysis and gasification of Victorian brown coal

Tao Xu, Joanne Tanner, Sankar Bhattacharya *

Department of Chemical Engineering, Monash University, VIC 3800, Australia
*Corresponding author. Email: Sankar.Bhattacharya@monash.edu

Extended Abstract

Victorian brown coal is an abundant, low-cost fuel largely used for power generation in Victoria. However, the issue of low efficiency and high greenhouse emissions have led to a larger focus on cleaner coal technologies. Coal gasification is one such technology which is being developed to use coal in a more efficient manner and allows for the possibility of producing liquid fuels and chemicals. Among the various types of available gasifiers, the entrained flow type provides the opportunity for high carbon conversion. Yet no information on entrained flow gasification of Victorian brown coal is available in the open literature. Our study is intended to fill this information void. While our current study explores entrained flow gasification over a wide temperature range from 700-1500°C, in this paper we focus on entrained flow gasification of Victorian brown coal and Chinese lignite in the low temperature range of 700-1000°C range. The experiments are carried out in an atmospheric pressure bench scale entrained flow gasification unit under the gasifying environment of 5-30% CO2 as the gasification agent, balanced with N2. The experiments use one acid-dried Victorian brown coal of 90-106 micron size. The effects of residence time, temperature and CO2 concentration on carbon conversion, fuel gas composition and gaseous pollutant emission are discussed in this paper. The experimental data generated in this study will be used for CFD modelling to assist in the development of the gasifier design and optimization of the gasification process in the temperature range of interest.

Keywords: entrained flow gasification, Victoria brown coal, residence time, carbon conversion.

Introduction

In Australia, Victorian brown coals represent a significant, low cost energy resource with reserves of 430 billion tonnes. However, its utilization is limited to mine-mouth power generation using conventional pulverized coal-fired combustion units at relatively low efficiencies [1]. Therefore, it is necessary to assess and develop alternative utilization techniques for this vast resource, such as gasification. Among different gasifiers, the entrained flow gasifier is attractive for commercial plants because of its feedstock flexibility and clean gas product. However, the technological information on brown coal gasification is limited. There has been one study reporting
on pressurized fluidized bed gasification of Victorian brown coals at a pilot scale, but the carbon conversion of Victorian brown coals is quite low[2].

In this study, information on the gasification behaviour of two Victorian brown coals, Yallourn (YL) and Morwell (MW) coal, is reported, including the release of alkali, sulphur, and chlorine species, carbon conversion, and gas quality during CO\textsubscript{2} gasification. The relation between 100% carbon conversion and residence time was investigated by regasifying the chars after every run of 5-6s residence time. This study generates fundamental information that will be useful for the design of commercial entrained-flow gasifiers using Victorian brown coals.

**Experimental**

The coal samples used in this study are Yallourn (YL) and Morwell (MW) coal, two Victorian brown coals from the Latrobe Valley, Victoria, Australia. For preparation of char, coal samples were grounded, air-dried, and sieved to 90-106 µm. Char was generated from the prepared samples by pyrolysis at 1000 °C in nitrogen in an entrained flow reactor.

An electrically heated entrained flow reactor was employed for the gasification experiments, as described elsewhere [3]. The furnace is of 2 m length and consists of six separately controllable heating zones. Solid products like ash and char residue was collected by a glass beaker connecting the quartz reactor. Product gas was measured by micro-GC after the cleaning system including water-ice boxes and the paper filter.

The experiments were conducted at various CO\textsubscript{2} concentrations (5% -20%), various temperature (700-1000 °C), and different residence time (6-24s) with a total gas flow rate of 5 L/min, to investigate their effect on gasification performance.

**Results and Discussion**

The temperature has significant effect on gas yield and gas quality during pyrolysis and CO\textsubscript{2} gasification of Victoria brown coals. It can be seen from figure 3(a) that the total yield of gaseous products increased with temperature under pyrolysis as a result of increased devolatilisation and decomposition of tar products. The changes in yield of the evolved pyrolysis gas components with temperature correspond to increased decomposition in the coal structure and gas phase cracking at higher temperatures. As the pyrolysis temperature was increased, the volume of hydrogen evolved in the gas phase increased due to increased structural decomposition and solid- and gas-phase ring condensation at higher temperatures. The yield of CO increased only slightly with increasing temperature, possibly due to the increased decomposition of oxygen-containing heterocyclic compounds, carbonyl groups and ether links.

Figure 3(b) also shows the influence of different temperatures on the gas composition, the CO concentration measured after 6s gasification of the YL char increased significantly from 1.64 vol% to 20.62 vol% with increasing reaction temperature from 700 °C to 1000 °C. Higher temperatures are known to enhance the endothermic Boudouard reaction (equation 5) and, as a result, more CO (20.62 vol%)
was generated at 1000 °C. As expected, the high temperature facilitated the Boudouard reaction thus improving the gas quality by increasing the CO percentage in the produced gas. With the comparison of CO concentration measured after 6s gasification of the YL char and the calculated value of equilibrium concentration under 20% CO2/80%N2 and various temperatures, the difference between them decreased with the increase of reaction temperature. It indicates lower residence time is needed for the char to obtain complete conversion at high temperature.

The influence of input CO2 concentration on composition of the produced gas at 1000 °C is shown in Figure 3 (a). As the CO is main product of CO2 gasification of coal, it is used to evaluate the effect of input CO2 concentration on gasification. It can be seen that produced CO yield with the increasing input CO2 concentration from 5 vol% to 20 vol% at 1000 °C. It indicates that increased reactant concentration resulted in an increase in the yield of CO from the Boudouard reaction.

The influence of residence time on the carbon conversion of Yallourn and Morwell coal char at an atmosphere of 20%CO2/80%N2 and 1000 °C was investigated, as well. From Figure 3 (b), the carbon conversion of YL steadily increased to 97.84 wt% when the residence time increased to 17.4 s. The carbon conversion increased only slightly from 97.8% to 99.1% with the increasing residence time from 17.4s to 23.4s. For Morwell char, with the increasing residence time, the carbon conversion also increased steadily from 46.5 wt% (5.2s) to 96.4 wt% (21.7s). The results indicate that for YL and MW char gasification under 20%CO2/80%N2 and 1000 °C, nearly 100% carbon conversion can be obtained at a minimum residence time of 17.4s and 21.7s, respectively. By comparing with Yallourn and Morwell char, Morwell coal char need 4 more second residence time than Yallourn coal char to obtain nearly 100% carbon conversion.

Figure 3: (a) influence of temperature on gas yield of MW coal in N2, (b) influence of temperature on gas quality of YL coal char in 20% CO2 (right)
Conclusions and recommendations

The experimental data establishes the residence time required for complete conversion of the YL and MW char at 1000 °C and 20% CO₂ to be 17.4s and 21.7s, respectively. An increase of reaction temperature resulted in an increase in gas yield of Victorian brown coals under pyrolysis and 20% 20% CO₂ gasification, due to the increased decomposition in the coal structure and gas phase cracking during pyrolysis process, and increased Boudouard reaction during CO₂ gasification. In terms of the effect of CO₂ input, the increased reactant gas resulted in a rise of CO gas yield from the Boudouard reaction.

In the future, the effect of higher temperature up to 1400 °C on carbon conversion and gas quality of Victorian brown coals need to be further investigated. More types of Victorian brown coal should get involved to compare in the study. The mineral transformation during entrained flow pyrolysis and gasification will be further investigated, as well.

Acknowledgements

The authors would like to gratefully acknowledge the support from China Scholarship Council, Brown Coal Innovation Australia (BCIA), and Monash University for their financial support.

References

Biography

Tao Xu is a 2nd year PhD candidate in the Department of Chemical Engineering at Monash University. He received his Bachelor Degree from Huazhong University of Science and Technology, Wuhan, China. He did his Master study at University of Waterloo, Ontario, Canada. His research mainly focuses on entrained-flow gasification behaviour of low rank coals and the mineral transformation during gasification process.
PROCESS SIMULATION AND EXERGY ANALYSIS FOR BROWN COAL PYROLYSIS AND GASIFICATION
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2Coal Chemical R&D Center of Kailuan Group, Kailuan Coal Minging Co Ltd, Tangshan, China.

Extended Abstract

Introduction
The Victorian brown coal (VBC) has a number of advantages such as large reserve, low-cost, high reactivity, low ash (less than 3 wt% on dry basis)[1]. However, the high moisture content up to 60-70% wt% (as received) is the largest barrier to restrict its utilization, which entails high transportation costs, potential safety hazards in transportation and storage, and the low thermal efficiency obtained in combustion of such coals[2]. This paper introduces a novel process for the utilisation of low-rank coal through the integration of pyrolysis and entrained-flow gasification by using Aspen Plus. In this process, an initial mild pyrolysis of the coal is proposed to simultaneously reduce the moisture content down to nearly zero and produce coal gas which has a similar property with gasification syngas. In this paper, the results for two typical brown coal samples were reported. The optimized conditions for their semi-coke gasification were clarified. The energy efficiency for such a system was analysed and compared to the traditional brown coal pre-drying system as well. The results show that higher exergy efficiency can be achieved for the proposed pyrolysis-gasification integration process.

Materials and Experimental
The flow sheet was build up by Aspen Plus version 8.4. The diagram of the process was shown in figure 1. Two typical kinds of brown coal, coal 1 (C1) and coal 2 (C2), were selected for this simulation. The feeding rate was fixed at 5000 kg/h. The gasification conditions was optimized. The exergy calculation was been conducted for the char, coal samples and then the exergy efficiency was been analysed for the whole process based on simulation results.
Results and Discussions

Figure 2 shows the variation of syngas composition as a function of temperature for the gasification of semi-coke derived from the pyrolysis unit. For both brown coal samples, the concentration of CO increases sharply before 1200°C and then remains stable when the temperature rises above 1300°C. Figure 3 provides the dependence of syngas composition on the variation of oxygen to carbon molar ratio (O/C). The syngas compositions are the values for the outlet of the gasifier. For both coal samples, the syngas molar flow experienced the same trend. It was found that the CO molar flow increases sharply with the increasing the O/C, and peaked at 1.0 at approximately stoichiometric ratio.

Table 1 illustrates the exergy analysis for both pre-drying gasification case and integrated pyrolysis gasification case for the two coal samples. As the results show, for both two coal samples, the products exergy from pyrolysis case is higher than their dry case. This is because the pyrolysis can achieve multi-valued products, including tar and methane. From the exergy destruction perspective, the exergy destruction in pyrolysis case is lower than the dry case. In light of this, the pyrolysis case is supervisor over the traditional pre-drying case.
Table 1 Exergy analysis for simulation process

<table>
<thead>
<tr>
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<th>E₁ (MW)</th>
<th>E₀ (MW)</th>
<th>Exergy destruction</th>
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<td>products</td>
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<tr>
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<td>C1-dry</td>
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<tr>
<td>C2-dry</td>
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<td>0.89</td>
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</table>

Conclusions
The appropriate temperature for brown coal entrained bed gasification should exceed 1300°C. The integrated pyrolysis-gasification process gives slightly less exergy destruction. The exergy efficiency for such a process is 3% higher than the pre-drying gasification process for coal 1, and 2% for coal 2.

Acknowledgements
The authors are grateful for the support from Monash University Institute of Graduate Research (MIGR) for the PhD. The authors are grateful for brown coal innovation Australia (BCIA) and Kai Luan coal chemical R&D centre for the financial support.

References

Biography
Baiqian Dai is a PhD student in Chemical engineering, Monash University. He is working on brown coal utilization, including blending combustion, gasification and ash characterisation.
Yield and quality of bio-oil produced from catalytic pyrolysis of microalgae using Ni/ZSM-5 catalysts

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Extended Abstract

Introduction
Pyrolysis is a pathway to produce biofuel from biomass. This involves the decomposition of organic compounds in the biomass in the absence of oxygen to produce gases, solid and liquids known as bio-oil. The bio-oil produced from pyrolysis process is unsuitable for use as transportation fuel and requires upgradation. One of the upgrading methods is in situ catalytic pyrolysis where the volatiles produced from microalgae are converted immediately by the catalyst in the same reactor. The number of studies on in situ catalytic pyrolysis of microalgae to produce bio-oil is still limited compared to lignocellulose biomass. This study involves the in situ catalytic pyrolysis of microalgae C.vulgaris for production of bio-oil. Ni/ZSM-5 catalysts used in this study were prepared by two different methods; ion exchange (IE) and wet impregnation (WI). The purpose of loading metal ion into the zeolite framework was to improve the activity of the catalyst to eliminate oxygenated compounds and increase the hydrocarbon yield. The pyrolysis experiment was conducted at different temperatures (300-600°C) and algae to catalyst ratios (5:1, 2:1, 1:1 and 1:2) to determine the yield and composition of bio-oil. The results showed that the catalyst preparation method does not affect the yield of bio-oil, but it does affect the bio-oil composition. Catalytic pyrolysis using Ni/ZSM-5 produced high hydrocarbon, less acid and O-compounds. In addition, less amount of catalyst required to improve the quality of bio-oil during catalytic pyrolysis of microalgae using Ni/ZSM-5 (IE) compared to Ni/ZSM-5 (WI). This paper presents the results from this experimental study. The results obtained will aid in the development of catalytic pyrolysis process in order to enhance the quality of bio-oil derived from microalgae.

Acknowledgements
The authors would like to thank Monash University for all the equipment provided in this experiment. Moreover, the authors also appreciated the work and help from undergraduate students, Sin Nin Neo and Yi Wen Loo.

Biography
Nur Hidayah Zainan received her Bachelor and Master degree in Biotechnology-Biochemical Engineering from International Islamic University, Malaysia in 2009
and 2012. She is currently receiving scholarship from Malaysian government to continue her PhD in Monash University, Australia.
**MICROWAVE PRE-TREATMENT OF LIGNOCELLULOSIC BIOMASS**

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**Extended Abstract**

**Introduction**

There has been a growing interest in the production of chemicals from environmentally friendly renewable biomass. A shift towards lignocellulosic feedstock has peaked in recent years and has been driven by a need to avoid the use of food resources. Lignocellulosic biomass has a complex structure which makes it difficult to convert into chemicals or biofuels [1]. There has yet to be a breakthrough on efficient methods for their transformation, in terms of cost and quality of product.

The results of an exploratory research project investigating the use of solvents and microwave irradiation to pre-treat Eucalyptus regnans sawdust to expose the sugars are described. Various dilute solvents at a reaction temperature of 180°C and various hold times were used. From the mild pre-treatment conditions used, it was found that approximately 20 to 50 mol% of the carbon 5 sugars were solubilized. Water showed the highest yield of carbon 5 sugars at 59.9 mol% at 30 minute hold time Ethylene glycol was used as a case study to investigate the correlation between the effect of microwave hold time and lignin-carbohydrate complexes formed on the surface of the remaining pre-treated fibres. The SEM images established that the number of complexes and their size increase with longer hold times.

**Materials and Experimental**

**Materials and Equipment:** *Eucalyptus regnans* sawdust and Spectrophotometric grade chemicals were used throughout the experiments. The QLab Pro Microwave Digester was used to heat the samples followed by the Agilent Technologies 1220 Infinity HPLC for analysis of reaction mixture.

**Experimental:** The sample was prepared by weighing out approximately 0.4 grams of eucalyptus sawdust using an analytical balance and transferred into a microwave vessel. A micro pipette was used to measure 9 mL of Milli-Q water and 1 mL of the desired solvent then transferred into the reaction vessel. The vessel was shaken to mix the contents and left for a few minutes prior to securing lid to prevent build-up of pressure. On completion of the experiment, the vessel was cooled to room temperature and taken out for analysis.
Results and Discussions

A number of dilute organic solvents were held for various times in the microwave at 180°C. The results for the pre-treatment using water are shown in Figure 1 below. A significant amount of carbon 5 sugars and furfural are produced over the various hold times. The reason behind this is that at high temperatures, water acts as an acid [2], thus providing an acidic environment that breaks down the lignin and hemicellulose and further degrading the carbon 5 sugars. From the solvents tested, water gave the best yield of carbon 5 sugars (59.9 mol%) at a 30 minute hold time. The pre-treatment only exposes a small amount of the carbon 6 sugars, which adds to the novel aspect of this process. The SEM images shown in Figure 2 compare a sample of raw sawdust against a sample of pre-treated sawdust. It is shown that the raw sawdust has a smooth surface with typical features present in wood, while the pre-treated sawdust has formed lignin-carbohydrate complexes on the surface. This phenomenon is believed to occur if the biomass is heated above 120°C [3].

Figure 2: Yield of desirable products with water as solvent at 180°C and various microwave hold times

Figure 3: (2a) Raw sawdust before pre-treatment, (2b) Pre-treated sawdust with 10 v/v% Ethylene Glycol, 5 minutes reaction time at 180°C
Conclusions
It was found that water produces the highest amount of carbon 5 sugars at a 30 minute hold time in the microwave digester at 180°C. As the reaction time increases, the amount of carbon 5 sugars produces start to degrade to the platform chemical furfural. The SEM images visualise the globules formed on the surface of the solid residue. This process makes for an efficient pre-treatment process as a significant amount of the hemicellulose and lignin are recovered in the solution, leaving the cellulose fibres behind.

Acknowledgements
- My supervisors; Akshat and Victoria
- Monash Centre of Electron Microscopy for their assistance with the SEM images.

References

Biography
Negin Amini completed her undergraduate double degree at RMIT University in Chemical Engineering and Applied Chemistry. The following year she obtained a Masters in Engineering Project Management from The University of Melbourne while simultaneously working in the chemical safety industry. She began her PhD at Monash University in 2014 and is working under the supervision of Dr Akshat Tanksale and Associate Professor Victoria Haritos on the project Microwave Pre-treatment of Lignocellulosic biomass.
CELLULOSE AEROGEL WITH TUNEABLE PORE STRUCTURE FOR OIL/WATER SEPARATION

Zhiyong He¹, Xiwang Zhang¹, Warren Batchelor¹
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Extended Abstract

Introduction

With the rapid industrial growth, such as in oil and gas, petrochemical, pharmaceutical, metallurgical and food processing industries, a large amount of oily wastewater is generated daily.¹ Current techniques for oil/water separation such as flotation and coagulation, are energy-intensive and require complicated machinery.² Besides, some of them are not applicable to the separation of oil/water emulsion.² Although traditional hydrophobic/oleophilic absorbent materials are used extensively in practical applications due to their low cost and ready availability, they are still faced with challenges, which are slowly moving researchers’ interest away from hydrophobic/oleophilic materials to hydrophilic/oleophobic materials in this application.² However, many existing hydrophilic/oleophobic materials are fabricated using petroleum-derived materials, and modified using harmful chemicals such as those with fluoride groups to gain oleophobic properties.³⁻⁶ Therefore, there is still large room for improvement to minimize their environmental impact.

Materials and Experimental

Micro fibrillated cellulose (MFC) purchased from DAICEL Chemical Industries Limited (Celish KY-100G) was used as the primary materials for preparing cellulose aerogel. MFC suspensions with various solids content mixed with calculated amount of PAE were prepared and poured slowly into 25ml beakers. They were then placed in freezer at -18°C for 24 hrs in order to maintain the porous structure. Thereafter, the frozen sponge-like aerogel was freeze-dried in freeze-dried for 24 hrs to remove all the moisture while maintaining its porous structure. Lastly, the freeze-dried samples were kept in oven at 120°C for 3 hrs to promote cross-linking.
Results and Discussions

![Graph showing oil rejection efficiency over cycles](image)

Fig. 1  (a) Separation efficiency of the cellulose aerogel to various oil/water layered mixture. (b) Experimental set-up for separation testing. (c) Comparison between emulsion (left) and filtrate collected (right). (d) & (e) Microscopic images of emulsion and filtrate collected, respectively.

Conclusions

In summary, we reported an oil/water separation process based on an aerogel produced using cellulose. The aerogel can be easily fabricated on a large scale by freeze-drying cellulose suspension, followed by cross-linking with PAE. With the super-hydrophilic and underwater super-oleophobic properties, excellent wet strength and pothole-like surface structure, it allows excellent oil/water separation efficiency to both oil/water mixture and oil/water surfactant-free emulsion. We also demonstrated that the pore structure of this aerogel can be easily engineered to potentially fulfil the need of separating oil-in-water emulsion with various droplet sizes while achieving an optimal fluid
flux. In addition, the separation was solely driven by gravitational force without any external power and additional facilities.

Acknowledgements
The authors acknowledged the use of facilities in Monash Centre for Electron Microscopy (MCEM). The research funds provide by The Bioprocessing Advanced Manufacturing Initiative (BAMI), the MGS and FEIPRS scholarships provided by Monash University.

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Biography
Zhiyong received his bachelor degree in Chemical Engineering (Hons) from Monash University, Clayton in 2013. In 2014 he became a PhD candidate at BioPRIA, under the supervision of Dr. Warren Batchelor and A/Prof. Xi Wang, working on oil/water separation using cellulose aerogel membrane.
PRODUCTION OF AGGLOMERATES VIA 3D PRINTING TECHNOLOGY FOR GRANULE BREAKAGE TEST

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2Institute of Particle Science and Engineering, University of Leeds, Leeds LS2 9JT, UK

Extended Abstract

Introduction
To improve the process design and end-product quality, it is essential to investigate the breakage behaviour of agglomerates [1]. Discrete Element Method (DEM) simulation is commonly used but is limited by the lack of identical, controlled agglomerates to test and validate simple models, let alone replicate the complex structure of real industrial agglomerates [2, 3]. This paper presents a novel 3D printing production method of test agglomerates with defined properties. Agglomerate models with different sizes and structures were designed using Solidworks 2014 software and printed by an Object500 Connex 3D printer. During the printing process, different digital materials were used to print the particles and the inter-particle bridges, allowing infinite combinations of bond strength, particle strength and agglomerate structure to be tested. Several different model agglomerates were printed at varying scales, using rigid polymer to print the spherical particles and ductile polymer to produce the inter-particle bridges. Preliminary compression tests were performed to compare the breakage behaviour of printed agglomerates. This 3D printing technique will allow more rigorous testing of agglomerate breakage models.

Materials and Experimental
A typical production process of agglomerates is shown in Figure 1. Agglomerate models were designed by Solidworks 2014 software. This model has 147 primary particles with a simple cubic structure (see Figure 1 a). Agglomerates were printed by an Objet 500 3D printer using rigid Verowhite material for the particles, and different flexible materials for the bonds (see Figure 1 b).

Results and Discussions
Compression tests were performed using Instron 5566 Universal Testing Machine, 1 mm/min cross head speed on agglomerates with 3 mm diameter primary particles. The preliminary compression curves showed good reproducibility (see Figure 2).
addition, the compression curves are obviously different in terms of different printing directions. The breakage process was also filmed as shown in Figure 2.

(a) Design by Solidworks  
(b) 3D printing process

Conclusions

This paper proposed a new 3D printing production method of agglomerates for breakage tests. The detailed process includes computer aided design, 3D printing and support material removal was illustrated. The compression breakage tests showed good reproducibility at same experimental conditions, and the influence of build directions were also addressed. In future, agglomerates with complex structures will be converted into 3D printed models, and then investigate how the material properties and structure influence the breakage behaviour.

Acknowledgements
This research project was supported by International Fine Particle Research Institute (IFPRI) and an ARC Discovery grant (DP150100119). Ruihuan Ge’s PhD scholarship was supported by the China Scholarship Council (CSC).

References


Biography

Ruihuan Ge received the BEng degree from Shandong University, Jinan, China, in 2011 and the MSc degree from the Institute of Thermophysics Engineering, Chinese Academy of Sciences, Beijing, China, in 2014. He is currently a PhD student in the Department of Chemical Engineering, Monash University, Melbourne, Australia. His current research interests include granule breakage, particle technology and 3D printing technology.
OPTIMISATION OF DETERGENT GRANULATION PROCESSES TO ACHIEVE RAPID DISSOLUTION OF PRODUCT AND REDUCE DRYING TIME

George Mutch¹, Karen Hapgood¹, Cordelia Selomuyla²

¹MAPEL
²Monash Food Technology Group

Extended Abstract

Introduction
The rate of dissolution of solid particles into liquid mixtures is of critical importance within a huge variety of industries producing consumer and industrial products, including: food, pharmaceuticals, paints, fertilizers and, most importantly for this study, detergents. Dissolution can severely affect production time of processes requiring a dissolution step in which raw materials provided as powder must be dissolved within a liquid phase. This is particularly important in the consumer chemicals industry where large scale blending of raw powder materials and liquid binders is relatively commonplace.

End-user requirements must be taken into consideration and for detergents the aim is often to achieve the most rapid dissolution to achieve a more effective wash cycle for clothes. However, most commercially available powder based detergent formulations are packaged and sold as granules, meaning that they comprise of a collection of primary particles bound together through cohesive properties and the formation of links or “bridges” between particles. Dissolving these granules is significantly more involved than dissolving individual particles partially due to the more complex mechanisms of dissolution which govern granule dissolution.

Figure 4: Algorithm for the optimisation of granule design.¹
Materials and Experimental

In order to achieve rapid dissolution the mechanisms by which particles dissolve must be thoroughly understood. Error! Reference source not found. shows an example algorithm proposed by Stepanek1 for the efficient design of granule microstructures to encourage dissolution. simulation refers to utilising computer algorithms to model the changes, physical and chemical, in granules over the course of the granulation.

The formulation is a key initial determinant of the processing structure and ideally process design should suit formulation rather than the other way around. Microstructure characterisation post-granulation provides one of the most important measures of end-user properties as the granule strength, dissolution rate and binder loading determine the efficacy of the product, resistance to degradation during transport, handling and storage and, if the product is a drug granule or other therapeutically active product, the toxicity. All these properties can be elucidated using post-granulation microstructure characterisation.

This study intends to further the current body of knowledge about the effects of varying formulations and processing conditions on the granule microstructure of detergent formulations. Of particular interest is the potential application of steady-state granulation and foam granulation technologies in the detergents industry to disperse viscous binders more efficiently2, narrow the size range of granules produced3,4 and hopefully lead to a rapidly dissolving product. Prior work has been conducted on foam granulation by Hapgood et al5–7 and has been shown to be effective at promoting binder dispersion more effectively than in the more traditional high shear wet granulation(HSWG) methods used by industry. Though these works were undertaken with respect to the pharmaceutical industry the concepts are relatively similar in drug formulations with high viscosity binders. This investigation will utilise lactose-MCC powder formulations to observe the effects of foam granulation, steady state and conventional HSWG on the dissolution rate of said granules. The dissolution tests will be conducted in a controlled environment assessed by fluorescence using Rhodamine B as a dye before bringing the data to the P&G innovation centre in Beijing to compare with the same tests run using pilot scale processes and P&G’s detergent formula. SEM images of the above granule microstructure will also be taken to observe correlations between granule geometry and dissolution rate.

Knowledge of these mechanisms underpinning reactive detergent granulation may allow for the design of a rapidly dissolving particle or granule through 3D printing techniques or computational experiments to suit a pre-existing production process or, if this proves too costly, to make adjustments to the system in order to empirically optimise the granule microstructure.
Results and Discussions & Conclusions
CURRENTLY NO SOLID DATA AVAILABLE

Acknowledgements
I would like to thank my supervisors Karen Hapgood and Cordelia Selomuyla for starting me off enthusiastically and of all the members of MAPEL and the Food Group for making me feel welcome as a first year PhD student.

References

Biography
I am a first year PhD student in the PACIA-GRIP program at Monash University. I completed my Bachelors’ double degree in Engineering (Hons) in the field of Chemical Engineering and Pharmaceutical Sciences. Across my academic career I’ve been involved with low temperature oxidation studies on lignite in the Green Chemistry Group at Monash and root cause analysis at Australian Paper Maryvale.
UNDERSTANDING PHARMACEUTICAL DRY POWDER BLENDING – IRON OXIDE TRACER BEHAVIOUR AND DIFFERENT EXCIPIENT POWDERS

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² Monash Institute of Pharmaceutical Science, Monash University, Royal Parade, Parkville, VIC, Australia.
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Extended Abstract

Introduction
Blending of one or more powders is critical for many pharmaceutical powders, including formulations used for Dry Powder Inhalers. Recent work [1] demonstrated that the colour change of an iron oxide tracer powder can be used to observe the mixing process and is linked to the quality of the mixing. The study used a 1wt% high purity Ferroxide® iron oxide in a range of lactose powders, and showed two key mixing stages linked to the total mixing energy applied and to the level of dispersion and deagglomeration of the tracer powder.

Materials and Experimental
This study extends the previous work by investigating whether the technique also can be used to examine the mixing behaviour of several common excipient powders (mannitol, MCC, methyl cellulose, PVP). For each experiment, 1 wt% of the tracer powder was added to 200-500g of the bulk excipient and blended in a 1L Key high shear mixer, samples were taken as a function of mixing time, and their colour readings in the CIELCh spectrum were recorded.

Results and Discussions
The results showed that most excipient powders show a similar overall behaviour pattern although the absolute colour values varied for each excipient as expected. For PVP and potassium chloride, however, it did not follow the same colour behaviour
due to the properties of the two powders.

In addition, four different coloured iron oxides grades were used to explore the behaviour of different colour oxides while blending with bulk lactose powder; 1 wt% of the iron oxide was mixed with the excipient lactose. Only the red iron oxides (hematite) showed the ability to change hue as mixing time/intensity increased: the yellow oxide (goethite) changed mainly with Chroma, and black oxide (magnetite) showed very little or no change in hue. The two grades of red iron oxide had different CIELCh spectrum values because of their overall colour but also due to their morphology and size.
Conclusions
The results show that the use of coloured tracer powder to track the progression of powder blending can be applied to a wide range of powders, and that more than one grade of red iron oxide displays the required change in hue. Further work is underway to understand the fundamentals of the hue change and determine whether there is a direct link between the blend colour points and the final product performance in dry powder inhaler formulations.

Acknowledgements
I would like to thank my supervisor Karen Hapgood, David Barling and my colleagues at MAPEL.

References

Biography
Kahlil Desai completed his double degree in chemistry and chemical engineering and also a diploma of German at Monash University in 2013. Kahlil has interned at GlaxoSmithKline (GSK) working with a pilot drum filter and optimising drum filters on-site. He is currently a second year PhD student investigating pharmaceutical powder blending especially in regards to dry powder inhaler (DPI) formulations used in asthma inhaler medication. His research is focused on using an iron oxide tracer to improve mixing quality and DPI efficiency, which would allow for a more design approach to pharmaceutical industry processes.
POLYSACCHARIDE-BASED NANOPARTICLE INTERACTIONS WITH THE IMMUNE SYSTEM
Liam Powles\textsuperscript{1}, Kirsty Wilson\textsuperscript{2}, Sue D. Xiang\textsuperscript{2}, Cordelia Selomulya\textsuperscript{1}, Magdalena Plebanski\textsuperscript{2}
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\textsuperscript{2}Department of Immunology, Monash University, Melbourne, VIC 3004

Extended Abstract

Introduction
In recent times vaccine research has focused on subunit and DNA vaccines in place of the attenuated/killed organism approaches used historically. While safer, with no chance of reversion to an infective form, these vaccines are generally less immunogenic and as such require boosting with adjuvants or delivery via a carrier to produce an immune response which can provide protection \cite{1}. Adjuvants can be defined as “any substance which when incorporated into a vaccine formulation acts generally to accelerate, prolong or enhance the quality of specific immune responses to vaccine antigens” \cite{2}. Conversely vaccine carriers or vectors are delivery systems to which the vaccine antigen can be linked to enhance its delivery to and uptake by antigen presenting cells (APCs), notably dendritic cells (DCs). The majority of vectors which have seen clinical study have been based on attenuated organisms such as genetically altered viruses. In recent years though more work has focused on synthetic vectors designed specifically for vaccine delivery. A synthetic carrier needs to be stable, affordable and scalable. Furthermore it should be biodegradable so it is easily removed from the body and non-toxic \cite{3}. Lastly, vaccines are required to induce specific types of immune responses depending on their target. For instance a vaccine against liver stage malarial infection should produce strong cytotoxic T cell responses along with a predominant Th1 helper response to remove infected cells \cite{4}. Therefore the natural immune response against a vaccine carrier needs to be understood so that it can be used to complement that induced by the vaccine. Pullulan coated iron oxide nanoparticles have been designed for use as vaccine carriers. Their interactions with antigen presenting cells and T cells have been analysed both \textit{in vitro} and \textit{in vivo} using flow cytometry.

Materials and Experimental

Mice: C57BL/6 mice were obtained from Monash Animal Services. The studies detailed here were approved by the AMREP animal ethics committee.

Materials: Pullulan based nanoparticles contain iron oxide and carboxymethylated pullulan. These were stored in DI water at 3.5\% solids and injected in PBS at 1\% solids. Complete RPMI supplemented with L-glutamine, 2-mercaptoethanol, fetal calf serum, HEPES and pen-strep. ACK lysis buffer, PBS, paraformaldehyde, perm buffer.
**Equipment:** BD LSR II 4 laser flow cytometer located in the AMREP flow facility.

**Procedure:** Bone Marrow Dendritic Cell (BMDC) culture – Bones from fore and back legs of three mice extracted after CO₂ cull. Bones flushed with complete media (CM) to extract marrow, red blood cells lysed and a single cell suspension created. Cells were cultured with GM-CSF for 3 days and particles added to a concentration of 80,000 and 800,000 particles per cell. Particles were incubated with cells for 24 hours and cells then harvested, washed, stained and measured via flow cytometry.

48 hour experiment: Particles at 1% solids were injected intradermally at the base of tail in 3 mice per group. After 48 hours the mice were culled and the spleens and draining lymph nodes harvested. The organs were mashed to extract cells, red blood cells in the spleen lysed and single cell suspensions created. Cells were stained in three different panels and measured via flow cytometry.

**Results and Discussions**

A BMDC culture was used to analyse the effect of particles on in vitro derived GM-CSF stimulated DCs and myeloid derived suppressor cells (MDSCs). The particles have no effect on the cell viability at either concentration. Small changes in the mean fluorescence intensities of the DC activation markers CD86, CD80 and PD-L1 imply that the particles are interacting with these cells. DC interactions were also evident in the spleen during the 48 hour experiment with CD40 levels increased on DCs and minor changes in CD80 and CD86 levels. Similar changes were not seen in the lymph nodes. A reduction in the ratio of CD11c-CD11b+GR-1hi/int MDSCs was seen in vitro and a reduction in the fraction of CD11c-CD11b+GR-1+ was evident in the spleen in vivo. This was associated with a decrease in the aforementioned ratio suggesting a reduction in the number of GR-1hi MDSCs. This is promising as...
MDSCs can suppress immune response development potentially inhibiting a vaccine response. Minimal variation was seen in the T regulatory cell population often linked to MDSC development and as such further analysis is required in this area. The MFI of CD69 on CD4+ T cells increased in the lymph node implying that at least some components of the particle were present in this organ and that they were to some degree immunogenic. Activation was also seen to a lesser extent in CD8+ T cells. In the spleen there was an increase in the percentage of CD4+ T cells correlated with a decrease in CD8+ T cells suggesting the particles interact to a greater degree with helper T cells. Further analysis of the transcription factor panel included in the study may help elucidate the phenotype of these T helper cells.

Conclusions
The pullulan based iron oxide nanoparticles clearly interact with both APCs and T cells in vitro and in vivo suggesting they are a viable vaccine carrier. While some results are clear, the interpretation of such is limited by the complexity inherent to the immune system. Continued analysis of the results will help elucidate potential mechanisms. Future experiments will attempt to determine the degree of particle uptake, which cells uptake the particles and the location at which uptake occurs in the body. The interactions between DCs stimulated with nanoparticles and T cells will also be probed.

Acknowledgements
Liam is supported by an APA scholarship. The project forms a part of interdisciplinary research activities between Chemical Engineering and Immunology, supported by ARC DP150101058. I would like to acknowledge the assistance of the VID lab with respect to data analysis.

References

Biography
Liam Powles is in the second year of his PhD in the department of chemical engineering at Monash University. His work is a collaboration between this department and the VID lab in the department of immunology. Prior to this he completed a double degree in chemical engineering and science (majoring in chemistry and mathematics) at Monash.
PREPARATION AND CHARACTERIZATION OF SILICA NANO PARTICLE-CELLULOSE NANOFIBRE COMPOSITES

Uthpala M. Garusinghe\textsuperscript{1}, Swambabu Varanasi\textsuperscript{1}, Gil Garnier\textsuperscript{1}, Warren Batchelor\textsuperscript{1}

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Extended Abstract

Introduction

Cellulose nanofibres are an exciting low-cost new organic materials. It is widely used due to the advantages such as flexibility, ductility, dielectric behaviour, processability, biodegradability and renewable in nature which replaces the conventional materials such as synthetic polymers\textsuperscript{(1, 2)}. Cellulose nanofibre sheets have exciting future prospects and applications such as tissue engineering\textsuperscript{(3)}, transparent conductive films for electronics, smart clothing\textsuperscript{(4)} and barriers\textsuperscript{(5)}. Nanofibre sheets alone have a limited range of porosity and surface area for a given furnish. Therefore, even though the commercial scale production of nanocellulose has not been completely achieved yet, the abundance of nanocellulose has given the researches to develop new organic/inorganic composite materials using nanocellulose as the main component. Such materials combine the advantages of both organic and inorganic phases and provide composites with for example high strength for barrier and packing applications. Challenges are still associated with production of nanocomposites. The restriction to large scale production and commercialization of nanocomposites is the cost effective dispersion of nanoparticles in the polymer. Microscale aggregations of nanoparticles cancel any benefits associated with nanoscale dimensions. Also, the absence of structure property relationships hinder nanocomposites been properly engineered.

In this study, we control both porosity and surface area of nanoparticle-nanofibre composites using microfibrillated cellulose (MFC) as the polymer matrix, silicon dioxide (SiO\textsubscript{2}) as nanoparticles and cationic polyacrylamides (CPAM) as the polymer to bridge nanoparticles and fibres together. Control simultaneous addition (CSA) method used in this paper gives a uniform distribution of nanoparticles within the matrix, avoiding any large scale aggregations which diminish the benefits associated with nanoscale dimensions. We also quantify the systematic behaviour in structure-property relationship of these composites.

Experimental procedure and characterization

Silica nanoparticle-cellulose nanofibre composite sheets were prepared by the addition of MFC, CPAM and SiO\textsubscript{2} using CSA method. CSA was conducted by 1) mixing SiO\textsubscript{2} (0.1wt \%) and CPAM (0.1wt \%) together, 2) mixing SiO\textsubscript{2}-CPAM mixture with MFC (0.1wt \%) mixture. The SiO\textsubscript{2} composition was varied between 10wt\% and 70wt\%. The effect of change in compositions were measured using mercury porosimetry and scanning electron microscopy (SEM) to obtain pore size.
distribution and morphology, respectively. The average particle size of SiO$_2$ and MFC was 125nm and 73nm respectively.

**Results and Discussions**

![SEM images of MFC-SiO$_2$ composites with different nanoparticle loadings at 30,000 magnifications. a) 10wt%, b) 40wt% and c) 60wt%.](image)

![Pore size distribution of MFC-SiO$_2$ composites with SiO$_2$ loading varying from 0-70wt%.](image)

At low nanoparticle loadings the pore structure is controlled by the agglomeration of the nanoparticles and their location in the pores between nanofibres (Figure 1a). As the loading increases, the structure of the composite changes. Figure 1b is the point at which the fibres start expanding to accommodate all the nanoparticles and particle agglomerates. At high nanoparticle loading the sheets behave as a packed bed, which consists of large network of uniformly packed nanoparticles, with much tighter control of pore size than at low levels of loading and very high surface area (Figure 1c). This can also be seen in pore size distribution results.

For pure MFC, single broad peak appeared within the range of 100-1000nm. As the loading increased, broad peak started disappearing while building up a sharp peak at the pore size range 30-50nm. This sharp peak continued to increase with higher loading. At 70wt% loading, the broad peak on right (Figure 2) disappeared completely. The pore size distribution as well was more uniform with a single sharp peak in the middle. This further proves that higher loadings give much tighter control.
of pore size and majority of the pore sizes are of same size. The disappearance of broad peak will make these composites of high loading to be used in applications where small pore sizes are necessary. The surface area of pure MFC sheet was measured to be 33 m$^2$/g while for 70 wt% loading sheet was 70 m$^2$/g.

**Conclusions**

Cellulose/inorganic nanocomposites were prepared using SiO$_2$ as the model nanoparticle. The structure of the composite clearly changed from a highly entangled network to a packed bed structure as the loading of SiO$_2$ increased. Mercury porosimetry results indicated that at 70 wt% loading, the composite consisted of mainly smaller pore sizes with much tighter control of pore sizes. Therefore, these composites with higher loadings can be used membrane applications where the pore size needs to be less than 100nm. Also, surface area of 70 wt% loading is much higher. If SiO$_2$ was replaced by a functionalised nanoparticles such as TiO$_2$, cellulose composite sheet with tremendous surface area from TiO$_2$ could be bring up interesting properties in purification aspect.

**Acknowledgements**

The author would like to acknowledge funding received for this project from BAMI ARC Industry Transformation Research Hub. The Author would also like to thank Monash University for FEIPRS and MGS scholarships.

**References**


**Biography**

Uthpala Garusinghe is a postgraduate student in the Department of Chemical Engineering. Her research focuses on the use of nanocellulose, nanoparticle and retention aids to produce novel composites and to engineer the structure-property relationships. She is working under the supervision of Doctor Warren Batchelor and Professor Gil Garnier.
**Extended Abstract**

**Introduction**

One dimensional TiO$_2$ rods has exhibited great photocatalytic activities[1], however this nanostructures has tendency to lie in the plane of the substrates is not favourable in photocatalytic activity[2]. Thus, grow TiO$_2$ rods directly on substract could resolve the problem. Treated TiO$_2$ rods with TiCl$_4$ can increase the surface area of the catalyst and reduce the pore size of the membrane. In this project, growing TiO$_2$ branched rod on the alumina disc in order to synthesis photocatalytic membrane. The synthesized membranes were examined in removing humic acid from wastewater.

**Materials and Experimental**

Firstly, the alumina discs were cleaned with acetone and water under sonication for 5 minutes before seeded with TiO$_2$ rods. 24 ml of aqueous HCl with concentration 16% was prepared and stir at room temperature for 5 min. After that, 0.4 ml of titanium butoxide was added into the solution and stir for another 5 min. The cleaned alumina disc was placed in a Teflon-lined autoclave and filled with the prepared solution. Hydrothermal process was taken place at 150°C for 20 h. To grow the branches on TiO$_2$ rods, the seeded alumina disc was placed in 0.2 M TiCl$_4$ aqueous. The bottle was sealed and kept at 25°C for 24 h. After that, the resulted membrane was calcined at 500°C with heating rate of 1°C/min for 2 h. The morphologies of TiO$_2$ branched rods photocatalytic membrane was observed using a scanning electron microscope (FEI Nova NanoSEM 450 FEG SEM). The crystal structure of the samples were examined using a X-ray diffractometer (Miniflex 600, Rigaku) with Cu Kα radiation at 40 kV and 20 mA over the 2θ range of 2 - 80°. The band gap energy of the as-prepared TiO$_2$ spheres was calculated using a band width spectrum recorded by a UV-vis spectrophotometer (UV-2600, Shimadzu). The performance of the prepared photocatalytic membrane was examined by using humic acid as pollutant.

**Results and Discussions**

As shown in Figure 1(a), the rods were grown and covered the surface of alumina disc. The thickness of the TiO$_2$ on the alumina disc was 12 μm. The rods on alumina disc were smooth and in the shape of cuboid with sides about 500 nm. After the TiO$_2$
rods were treated with TiCl₄, clearly showed that the smooth surface has turned rough surface (Figure 1 (f)). Very small TiO₂ nanoparticles were grown on the rod as seen in high magnification of SEM image in Figure 1 (g).

Figure 1: SEM images of (a-c) top view of TiO₂ cuboid photocatalytic membrane; (d) cross section view of TiO₂ cuboid photocatalytic membrane; (e-g) top view of TiO₂ branched cuboid photocatalytic membrane; (h) cross section

The XRD pattern in figure 2 (a) shows that TiO₂ branched cuboid was pure rutile phase and it was confirmed by TEM high magnification image in Figure 1 (l). The fringe lattices in Figure 1 (j) and (l) were 0.313 nm and 0.23 nm, which represented (110) and (200) planes for rutile phase. On the other hand, the bandgap energy of TiO₂ branched cuboid was narrowed to 2.9 eV compared to 3.2 eV to P25. Greater light of adsorption of TiO₂ branched cuboid in the visible light range was demonstrated in Figure 2 (b). Figure 1 (i) shows the TEM images of single cuboid of TiO₂ with smooth surface. However after the TiCl₄ treatment, lots of small TiO₂ particles were attached on the cuboid as shown in figure 1 (k).
Figure 2: (a) XRD pattern of TiO$_2$ branched cuboid compared with alumina disc; (b) UV-vis absorbance spectra of TiO$_2$ branched cuboid compared with alumina disc and P25; (c) Flux of TiO$_2$ branched cuboid photocatalytic membrane.

The as-prepared membrane was performed very good in removing humic acid under illumination of UV light. It could remove 82% of humic acid and recover the effluent flux when the UV light was turned on throughout the filtration process as seen in Figure 2 (c). The green colour on the graph shows that the UV light was turned on for 15 min during the filtration process.

**Conclusions**

TiO$_2$ branched rod photocatalytic membrane was successfully synthesized in this project. The synthesized membrane shows its ability to recover the flux under irradiation of UV light. Furthermore, it could remove 82% of humic acid from the wastewater.

**Acknowledgements**

The authors acknowledge use of the facilities at the Monash Centre for Electron Microscopy.

**References**


**Biography**

Sookwan Leong is a PhD candidate under supervision of Prof. Huanting Wang and Prof. Karen Hapgood. Her research is focusing on developing novel photocatalyst incorporating membrane technology to remove pollutants from wastewater.
LIGHT AND PERSPIRATION STABILITY OF TRIAZINYLSSTILBENE FLUORESCENT BRIGHTENERS ON COTTON FABRICS

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\textsuperscript{2} Monash University, Melbourne, Australia

Extended Abstract

Introduction
Triazinylstilbene fluorescent brighteners (TFBs), which account for more than 80% of the commercial whitening agents, are widely used for the finishing process of cotton fabrics [1]. The fading of TFBs on cellulose matrix under simultaneous exposure to sunlight and human sweat may reduce the visual quality of garment, as well as producing toxic substances which directly contact skin [2]. Nowadays, as a result of steady improvement of living standard, the light and perspiration stability of textiles, especially for cotton fabric commonly employed in summer, has increasingly attracted consumer attention. Therefore, the light and perspiration (L-P) stability of TFBs on cotton fabrics has become essential and important.

Materials and Experimental
Bleached plain woven cotton fabric and six TFBs (Figure 1 and Table 1) were used. The artificial perspirations were prepared according to Association for Textile Technical Study (ATTS) standard and American Association of Textile Chemists and Colorists (AATCC) standard. Single sweat component solution (105% o.w.f.) and the perspiration (105% o.w.f) were evenly dripped on the surface of whitened cotton fabrics, before which were promptly placed in the XENOTEST150S+ light fastness test instrument. The fabrics exposed to the simulated daylight under the dry condition were set as the control group. The temperature and the relative humidity were controlled at 35 °C and 40%, respectively. Subsequently, samples were exposed to the simulated sunlight from a 1500W xenon-arc lamp for 30 h. The whiteness variation percentage (W.V.P.) was used as a measure of the photo-fading of cotton fabric detected with the Datacolor SF650 and calculated using the following formula:

\[ W.V.P = \left( \frac{W_0 - W_t}{W_0} \right) \times 100\% \]  

where \( W_0 \) and \( W_t \) are the whiteness fabrics before and after irradiation, respectively.

![Figure 1 Basic structure of TFBs](image)

Table 1 Substituent groups in the molecular of TFBs
Results and Discussions

Figure 2 demonstrates that the L-P stability of TFBs on cotton fabrics is influenced by substituent groups and artificial perspirations dramatically. The L-P stability of TFBs is reduced by morpholine group, while improved by the extra sulfonic groups and diethanolamine group. Among three selected standards of artificial perspiration, the alkaline sweat of ATTS is considered as the maximum retarding affecting factor on the light stability of TFBs. The TFB with imino group (-NH-) on triazine exhibits better light stability under the AATCC standard than that of acidic ATTS, which is reversed in the TFB with extra sulfonic acid group on its aniline structure.

![Figure 2 The W.V.P of selected TFBs under the three standard artificial perspirations and the control condition](image)

The light stability of TFBs is affected by perspiration components (Figure 3). The effect of lactic acid is induced by the interaction of two factors, which is depended on its pH value. The decrease of pH value leads to the protonation of TFBs on cotton fabrics, reducing its fluorescence intensity, while increase of pH value suppresses the lactic acid evoked protonation of TFBs, with the lactic acid playing the counterbalance effect on the photo-oxidation of TFBs [1]. However, the amino acids including L-histidine and DL-aspartic acids quenched the fluorescent of TFBs by competitive adsorption effect as well as activating the oxygen. In contrast, the sodium salt compounds in the artificial perspiration composed of sodium chloride, disodium

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hydrogen phosphate and sodium D-pantothenic restrained the photo-reaction of TFBs on cellulose fibers by forming the sandwich-like complex.

![Graph showing W.V.Ps of cotton treated with TFBs under different conditions exposed to light for 30h](image)

**Figure 3** The W.V.Ps of the cottons treated with TFBs under different conditions exposed to the light for 30h

**Conclusions**

The effects of components vary with artificial perspirations. In the alkaline ATTS standard, reducibility of lactic acid plays the counterbalance effect on the photo-oxidation of TFBs, and the competitive adsorption effect of L-histidine is suppressed. Nevertheless, in the acidic perspirations of ATTS and AATCC standards, reducibility of lactic acid is counteracted by its protonation effect on TFBs, reducing the light stability of TFBs significantly. Meanwhile, the competitive adsorption effect of L-histidine promotes desorption of TFBs. In addition, the aggregation induced by sodium chloride and producing of sandwich-like complexes caused by compounds containing sodium play the synergistic inhibition effect on photo-fading of TFBs on cotton fabrics under both of perspirations of ATTS and AATCC standards.

**Acknowledgements**

R.Y. Chen thank Monash University Institute of Graduate Research and the Faculty of Engineering for postgraduate research scholarships.

**References**


**Biography**

Ruoyang Chen was born in China in 1988. He received an M.E. in Textile Chemistry and Dyeing and Finishing Engineering from Donghua University. He researched on the light and perspiration stability of triazinylstilbene fluorescent brighteners. Currently, he is a Ph.D. student in Chemical Engineering at Monash University, working under Professor Wei Shen.
MODIFICATION OF AN ASYMMETRIC POROUS POLYMER FOR HIGH GAS PERFORMANCE ZIF-8 MEMBRANE
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Introduction

Metal organic framework (MOF) membranes and thin films used for gas separation have been receiving considerable attention. Although various ceramic substrates have been used to prepare MOF membranes so far, high cost and processing difficulties of the support materials may limit their industrial applications. Growing MOFs on polymer membranes can effectively solve these problems and therefore MOF polymer membranes are greatly in demand [1]. Here, we demonstrate the synthesis of ZIF-8 on the asymmetric porous bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) substrate based on support ethylenediamine (EDA) vapour-phase surface modification and fast, in situ growth. EDA-vapour has the advantages of surface-restrictive modifications, nominal swelling effect, the reusability of original EDA for economic concerns, and room temperature modification process. EDA effectively tightens the polymer network, improves the membrane dimensional stability and also acts as covalent link between the growing ZIF-8 crystals and the support. This produces a large number of nucleation sites for the growth of ZIF-8 layer on the asymmetric porous support. Our simultaneous surface chemistry and pore structure modification combined with the fast in situ method results in extremely thin (~300 nm), continuous and defect-free ZIF-8 membranes, exhibiting both ideal selectivities (H₂/CO₂: 12.8; H₂/N₂: 9.8) and permeance (20.5× 10⁻⁷ mol.m⁻².s⁻¹.Pa⁻¹) higher than those reported in literature for flexible polymer-supported ZIF-8 membranes.

Materials and Experimental

For formation of the ZIF-8 layer, the vapour-phase-EDA-modified BPPO support was immersed vertically in a solution of zinc acetate dehydrate (0.22 g) in 9.6 g methanol and sonicated for 3 min. A solution of Hmim (0.164 g) in 9.6 g methanol was added to the above solution, followed by dropwise addition of ammonium hydroxide solution (0.12 g), and the mixture was then ultrasonically treated for another 3 min. After crystallization at room temperature, the ZIF-8@BPPO composite membranes were washed with methanol and dried.

Results and Discussions

Figure 1a shows the method developed in this work. The chemical reaction between the BPPO support and EDA vapour during the modification was determined using the
FTIR-ATR technique and the results are shown in Figure 1b. The pristine BPPO has IR bands at around 586 cm$^{-1}$ and 633 cm$^{-1}$, which are attributed to the benzyl bromide (−CH$_2$Br) groups (C−Br stretching). After EDA-vapour modification, these bands almost disappear and a new broad band in the range of ~3100-3600 cm$^{-1}$ emerges, which is ascribed to the N−H stretching and confirms the amination of BPPO.

Figure 1: (a) Schematic diagram of the preparation of a BPPO polymer supported ZIF-8 membrane; (b) FTIR ATR spectra of the untreated BPPO support, BPPO modified with EDA-vapour for 16 h (MBPPO), MBPPO supported ZIF-8 layer (ZIF@8-MBPPO), and synthesized ZIF-8 powder.

After the substrate modification, an ultrathin ZIF-8 membrane of about 200 nm is formed on top of the polymer support (Figure 2a, b). The top-view image (Figure 2a) shows that the support surface was covered entirely with a continuous and compact ZIF-8 layer without any visible defects such as pinholes or cracks.

ZIF-8@BPPO composite membranes prepared with 16 hour amination times show excellent gas selectivities. ZIF-8@BPPO exhibited H$_2$/CO$_2$ and H$_2$/N$_2$ ideal selectivities of 12.8 and 9.7 (inset in Figure 2c), respectively; it also had H$_2$ permeance as high as 2.05 × 10$^{-6}$ mol.m$^{-2}$.s$^{-1}$.Pa$^{-1}$ (Figure 2c). This membrane is amongst the best ZIF-8 membranes reported previously. For instance, at a similar H$_2$/N$_2$ selectivity, the ZIF-8 membrane prepared in this study had two orders of magnitude higher H$_2$ gas permeance than those prepared by the epitaxy method.

Figure 2: SEM images of the (a) surface and (b) cross-section of the ZIF-8@MBPPO; (c) Single gas permeances of ZIF-8@MBPPO as a function of kinetic diameter of gas molecules.

Conclusions
In summary, we have successfully prepared a compact, ultra-thin ZIF-8 layer on an asymmetric polymeric substrate by chemical vapour modification of the surface
chemistry and pore structure. The thickness of the membrane fabricated here is one of the thinnest ever reported. The reproducibly prepared ZIF-8 membrane exhibits ideal selectivities (H₂/CO₂: 12.8; H₂/N₂: 9.8) and permeance (2.05×10⁻⁶ mol.m⁻².s⁻¹.Pa⁻¹) which is among the highest reported so far. The proposed chemical vapour modification followed by fast in situ synthesis provides a rapid, convenient and effective route for preparing thin yet continuous and defect free ZIF membranes on the surface of polymeric substrates.

**Acknowledgements**

This work is in part supported by the Australian Research Council (Project no. DP140101591). The authors acknowledge use of the facilities and the assistance of Xi-Ya Fang, Kathryn Waldron and Flame Burgmann at the Monash Centre for Electron Microscopy. E.S. thanks Monash University for MGS and FEIPRS scholarship. H.W. thanks ARC for a Future Fellowship (Project No. FT100100192).

**References**


**Biography**

Ezzatollah Shamsaei has a Master degree in Chemical Engineering from University of Technology, Malaysia and a Bachelor degree in Science (Chemistry) from Arak University, Iran. He is currently a third-year PhD student under supervision of Prof Huanling Wang and Dr Zhe Liu in the Department of Chemical Engineering, Monash University. His research is focused on the development of composite membranes for water treatment and gas separation.
COPPER NANOWIRES AS CONDUCTIVE INK FOR LOW COST DRAW-ON ELECTRONICS

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Extended Abstract

Introduction

This work tackles the complicated problem of clump formation and entanglement of high aspect ratio copper nanowires, due to which a well dispersed solution for use as a true ink for drawable electronics has not been made until now. Through rheology studies even a hard to use material like copper nanowires was tailored to be made into a highly efficient conductive ink with only 2 vol % or 18.28 wt% loading which is far lower than existing nanoparticle based inks. This versatile ink can be applied onto various substrates such as paper, PET, PDMS and latex. By using the ink in a roller ball pen, a bending sensor device was simply drawn on paper, which demonstrated detection of various degrees of convex bending and was highly durable as shown in the 10,000 bending cycling test. A highly sensitive strain sensor which has a maximum gauge factor of 54.38 was also fabricated by simply painting the ink onto latex rubber strip using a paintbrush. Finally a complex conductive pattern depicting the Sydney Opera House was painted on paper to demonstrate the versatility and robustness of the ink. The use of Cu NWs is highly economical in terms of the conductive filler loading in the ink and the cost of copper itself as compared to other metal NPs, CNT, and graphene-based inks. The demonstrated e-ink, devices, and facile device fabrication methods push the field one step closer to truly creating cheap and highly reliable skin like devices “on the fly”.

Materials and Experimental

Materials. Hexadecylamine (HDA) Sigma-Aldrich, copper chloride (CuCl₂·2H₂O) Sigma-Aldrich, D-glucose (α or β) Merck, hydroxypropyl cellulose (HPC) Sigma-Aldrich, 20 mesh, Mw = 1 000 000.

Cu NWs Synthesis. Our Cu NWs were synthesized using a scaled up amine-capped and glucose-based reduction method. An oil bath was preheated to 100 °C, into which a screw cap borosilicate bottle with 50 mL of water, was immersed. When bubbles began to appear in the water then 900 mg of hexadecylamine (HDA) (Sigma-Aldrich) and 100 mg of copper chloride (CuCl₂·2H₂O)(Sigma-Aldrich) were added and stirred for 30 min at 1000 rpm. The solution would have turned a homogeneous sky blue color, then 500 mg of D-glucose (α or β) (Merck) was added to it, the stirring speed was reduced to 400 rpm and the reaction was allowed to run for 6 h, then stopped. After the addition of glucose the solution changed color from pale brown to dark brown. The reaction solution was removed from the oil bath and
allowed to cool for 10 min after which it was centrifuged at 6500 rpm for 5 min. The Cu NWs were collected at the bottom of the tubes as a neat pellet, which can be easily recovered by carefully decanting the supernatant and gently rinsing the pellet with Mili-Q water a few times.

**Cu NWs Ink Formulation.** After careful rheology studies it has been found that for every 1 g (wet pellet weight) of Cu NWs, 9.468 mg of HPC is needed to well suspend them. The ink was diluted with Mili-Q water to make a 2.2 mL final ink solution.

**Results and Discussions**

![Figure 1](image.png)

Figure 1. (a) Optical image of Cu NWs ink, (b) TEM image showing diameter, (c) SEM image showing percolation network, (d) Cu NWs concentration vs shear viscosity at 80/s shear rate, and (e) Cu NWs concentration vs resistance at 3 concentrations obtained from shear viscosity chart; 0.2, 1, 2 vol %. Insets show optical image.

**Conclusions**

In conclusion, we showed that the roller-ball ink delivery approach is well suited for porous, not too rough, absorbent substrates like paper, that is, surfaces for which the
ball-point pen has been designed. For smooth but comparatively soft substrates like PDMS and latex rubber, the paintbrush approach is a better option. It is noteworthy that the way in which a NP-based ink trace forms a percolation network is very different to the way a NW-based ink trace does; hence, these unique problems. Nonetheless, we have demonstrated that even a hard to use material like Cu NWs can be tailored to be made into a conductive ink with a variety of applications. It is also demonstrated in this work that due to the use of high aspect ratio NWs instead of NPs, we are able to deliver a conductive trace onto a nonuniform substrate, such as coated paper, and even paint a conductive pattern of the Sydney Opera House. These drawable Cu NWs traces exhibited reasonably high stability under ambient conditions. The use of Cu NWs is highly economical in terms of the conductive filler loading in the ink and the cost of copper itself as compared to other metal NPs, CNT, and graphene-based inks. The demonstrated e-ink, devices, and facile device fabrication methods push the field one step closer to truly creating cheap and highly reliable skin-like devices “on the fly”.

Acknowledgements
This work is financially supported by Australia Discovery Projects DP140100052 and DP150103750. The authors thank the Monash Center for Electron Microscopy facilities (MCEM) for the generous use of the FEI Nova NanoSEM 450 FESEM, FEI Tecnai T20 TEM. We also acknowledge the use of the research facilities at the Melbourne Centre for Nanofabrication. N.N.J. also thanks Monash University for the graduate student scholarship (MGS) and the Victorian government for the Victorian International Research Scholarship (VIRS).

Biography
Naveen Noah Jason is a PhD student working on the fabrication of flexible and wearable electronics using nanomaterials. He previously obtained his Masters degree in Chemical Engineering from the National Institute of Technology, Rourkela, India and his Bachelors from Indira Gandhi Institute of Technology, Sarang, India. He loves the outdoors very much, bushwalking and music are his favourite interests.
VOLUME-IN Variant IONIC LIQUIDS MICROBANDS AS HIGHLY DURABLE WEARABLE BIOMEDICAL SENSORS

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Extended Abstract

Introduction
Most current wearable electronic products are often based on rigid circuit board technologies, limiting their ‘true wearability’ on the soft human body due to the mechanical mismatch between electronic and biological materials.1-6 ‘True wearability’, which means intimate contact with the soft human body, can only really be achieved by stretchable electronics that can mimic the mechanical features of the human skin. The use of nanomaterials or wavy metal/semiconductor materials represents a promising strategy to achieve stretchable electronic devices, but often experience local material delamination or cracking.7 In this work, we describe an ionic liquid (IL)-based approach to fabricate rubber band-like, stretchable strain sensors, which can circumvent these limitations. Non-volatile and flow properties allow us simply to ‘fill and seal’ microchannels fabricated by 3D printing to obtain lightweight, waterproof and thermally-sensitive wearable sensors. Despite the simplicity in fabrication, the sensors show excellent performance, including tuneable sensitivity, detection of a wide range of strains (0.1% - 500%), high durability (little change in signal-to-noise ratios after 6 month storage under ambient conditions), excellent long-term stability of 50,000 life cycles under both low (5%) and high (100%) strain. We further show that our IL-based sensor can accurately identify wrist pulses, and can be woven with commercial rubber bands into colourful bracelets for

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hand gesture detection, and seamlessly interface with wireless circuitry for detecting cervical movements.

**Materials and Experimental**

Device fabrication: The design of the 3D printing mould using 3D Max was undertaken and the resultant mould printed by a 3D printer (Objet Eden 360). The materials used for printing is Fullcure 720. The Ecoflex curable silicone fluid was poured into the printed mold and cured for 1 hour under 60°C after which it was peeled off. The grooves in the silicone were then filled with ILs and conductive wires affixed. Following this, a layer of cured Ecoflex was coated on the surface to encapsulate the grooves after spreading a liquid layer of Ecoflex. This assembly was trimmed and cut to make a well-shaped rubber band sensor.

**Results and Discussions**

![Figure 1. Real-time monitoring of wrist pulses, hand gestures and cervical movements.](image)

**Conclusion**

Our sensor could detect finely and widely the strains as small as 0.1% and as high as 500%. The sensor is highly durable, thermally-sensitive, exhibiting excellent performance in cycling, aging and water tests. We also show that the sensitivity of the
sensors could be tuned simply by adjusting the microchannel widths. These attributes enabled the real-time detectability of subtle strains from artery wrist pulse, and large strains from various different hand gestures. Furthermore, we demonstrated the wireless sensing system for the cervical movement monitoring. We believe this IL-based strategy opens a new powerful methodology in the design of low-cost wearable sensors.

**Acknowledgements**

This work is financially supported by ARC Discovery projects DP120100170 and DP150103750. This work was performed in part at the Melbourne Centre for Nanofabrication (MCN) in the Victorian Node of the Australian National Fabrication Facility (ANFF) and the ITIDLab (International Tangible Interaction Design Lab) in Monash University.

**Reference**


**Biography:** Joined in Wenlong Cheng’s group as postgraduate student in September 2014. Research project focuses on stretchable electronics based on ionic liquids and 3D printing.
POST-SYNTHETIC Ti EXCHANGED UiO-66; ENHANCING THE PERFORMANCE AND INDUSTRIAL RELEVANCE OF UNSUPPORTED METAL ORGANIC FRAMEWORK MIXED MATRIX MEMBRANES

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Extended Abstract

Introduction
Membranes offer one of the lowest energy routes to carbon dioxide separation from flue gas.1 Key to handling the immense scale of Carbon Capture separations is achieving maximum membrane permeability while retaining sufficient selectivity for CO2 over N2. Mixed matrix membranes (MMM) offer an exciting potential to enhance separation performance over pure polymers, however also generate additional complications for optimizing their performance and feasibility for industrial implementation.

As we recently reported,2 metals can be post-synthetically exchanged in Metal-Organic Frameworks (MOFs) to drastically enhance gas transport performance in mixed matrix membranes. Ti-exchanged UiO-66 MOFs were found to triple CO2 gas permeability without a loss in selectivity. As a result, it is also shown that MOFs optimized in previous works3 for batch-wise adsorption applications can be applied to membranes, which have lower demands on material quantities. These Ti-exchanged membranes exhibit exceptional CO2 permeability enhancement of as much as 153% when compared to the non-exchanged UiO-66 mixed-matrix membrane controls, which places them well above the Robeson upper bound at 5 wt.% loading. Maximum permeability enhancement occurs at very low loadings, significantly less than the optimum for other MMMs, and is a major advantage for large-scale application due to the more attainable quantities of MOF required. Additionally, Ti exchange also had a significant effect in improving the mechanical properties of prepared films, exhibiting greater or higher mechanical stability over 3 months.

Materials and Experimental
Ti-MOFs were prepared post-synthetic exchange of Titanium into the Zirconium based UiO-66 MOF3. These Ti exchanged MOFs were impregnated into a Polymer of Intrinsic Microporosity (PIM-1) to examine whether the enhanced adsorption properties (81% increase in CO2 uptake) would correlate to improved membrane performance.2 A range of Ti$_x$UiO-66, where x represents the exchange period in days, were prepared to examine the effects of loading and degree of exchange on the
gas separation performance of TixUiO-66 PIM-1 nanocomposites. The resulting nanocomposites were consequently characterised to induce the mechanism responsible for the exceptional gas permeability and mechanical properties over the native polymer.

**Results and Discussions**

As hypothesized, addition of Ti-MOFS generated an exceptional increase in CO2 permeability, the highest increasing 274% over the virgin film, and 153% over the equivalently loaded UiO-66 membrane (Figure 1A). When plotted against the Robeson Upper Bound,4 the remarkable permeability of the 5 wt. % Ti,U UiO-66 loaded films is clear, with each exceeding the trade-off boundary (Figure 1B).

![Figure 10: (Left) CO2 Permeability of PIM-1 Ti,U UiO-66 mixed matrix membranes. Image source.](image1)

![Figure 2: (Right) PIM-1 Ti,U UiO-66 (5 wt.%) membranes plotted against the Robeson Upper Bound. Lines highlight trends of inclusion loading and Ti exchange. Image source.](image2)

The range of TixUiO-66 MOFs and membrane loadings provided a matrix to examine the factors behind the drastically enhanced performance. Generally, addition of MOFs reduced the solubility of the polymer membrane, but was compensated by a large increase in membrane diffusivity. Ti exchange caused a further increase in Solubility and Diffusivity in films over the equivalent UiO-66 film. Permeability enhancement was lost at higher loadings due to agglomeration and gradual crystallinity loss of longer exchanged Ti,U UiO-66. As expected, the trend in increased in fractional free volume, mirrors that of the permeability enhancement, however doesn’t account for the further enhancement upon transmetalation with Ti. As the exchange progresses, it appears some of the linkers are lost exposing surface metal sites to polymer interaction. Polymer-MOF interaction, measured by DSC and solution viscosity consistently increases while gradually decomposition of the porous MOF lattice accounts for reduction in membrane performance observed after 5 days of exchange.

The addition of Ti,U UiO-66 also reduced the rate of permeability loss from physical aging, improving the films suitability for application. However, more interestingly, Ti-MOF 10 wt.% mixed matrix films displayed improved mechanical properties as
well. Stress as Strain was maintained at the level of the pure polymer, however over time the polymer’s embrittlement from physical aging and free volume collapse resulted in the Ti\textsubscript{5}UiO-66 nanocomposite was stronger than the native polymer film. The increased polymer interaction with Ti-exchanged MOFs polymer stabilises the film against the added defects with the film and from mechanical degradation due to physical aging of the glassy polymer matrix.

Conclusions
Mixed Matrix Membranes have the potential to generate significant performance improvements, however other factors affecting implementation; including quantities required, service life, and mechanical properties, also require careful consideration. Our work shows Post Synthesis Exchange of MOFs can greatly enhance membrane performance with as little as 5 wt. % additive, a major advantage over other MOF-based separation processes. Additionally, Ti-MOF composites exhibit improved mechanical properties and reduced embrittlement with aging over the pure polymer and un-exchanged composites. The polymer-additive interaction is a determining factor behind many of the key characteristics required for improvements to mixed matrix membranes and further research should greatly assist overcoming the barriers faced by industrial implementation of MMM technology.

Acknowledgements
This research was supported by the Science and Industry Endowment Fund (SIEF)

References

Biography
Stefan commenced PhD study in 2013 under the collaborative supervision of Associate Professor Bradley Ladewig, of Monash University (now Imperial College),
and Dr Matthew Hill and Dr Cher Hon Lau of CSIRO. Stefan’s work centers on the development of super glassy polymer nanocomposite membranes, using MOFs and other porous frameworks. His research aims to tune the polymer-particle interaction to optimise separation performance, mechanical properties, and understand its affect on aging; key factors to the application of nanocomposite membranes to industrial processes. Recently, Stefan’s initial work on high performance Mixed Matrix Membranes containing Titanium exchanged Metal-Organic Frameworks was published by Scientific Reports.
ENGINEERING THE COLLOIDAL STRUCTURE OF NANOCELLULOSE FIBRES USING POLYMERS TO CONTROL FILTRATION AND SHEET PROPERTIES
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Introduction
This study examines and quantifies the effect of adding polyelectrolytes to nanocellulose suspensions on the gel point, which is the lowest solids concentration at which the suspension forms a continuous network [1]. We developed a master curve which showed that the independent variable controlling the behaviour of nanocellulose suspensions and its composite is the structure of the flocculated suspension which is best quantified as the gel point. This was independent of the type of polyelectrolyte used. There was no significant difference in the minimum gel point achieved, despite the difference in polyelectrolyte morphology and molecular weight. A lower gel point makes it easier for water to drain through the fibre network, reducing the pressure required to achieve a given dewatering rate and reducing the drainage time required to form a wet laid sheet. We also showed that the lower gel point, partially controls the structure of the wet laid sheet after it is dried. Halving the gel point increased the air permeability of the dry sheet by 37%, 46% and 25%, when using CPAM, HPEI and LPEI, respectively. This study showed that the sheet forming process conditions and final sheet properties can be engineered by adding polyelectrolytes to the nanocellulose suspension.

Materials and Experimental
Microfibrillated cellulose (MFC) was purchased from Daicel Chemical Industries Limited. Polyethyleneimine (PEI) solution of molecular weight of 750kDa and 1.8 kDa were denoted as HPEI and LPEI, respectively. The cationic polyacrylamide (CPAM) polymer used has 40% charge and is of molecular weight 13MDa.

250mL of nanocellulose suspension with solids concentration (=solids fraction × suspension density) ranging from 0.1wt% to 0.01wt% were prepared. The suspension was agitated before the polymer solution was added to it at the required addition level. The nanocellulose-polymer suspension was then agitated again and poured into a measuring cylinder. After 48 hours, the final sediment height was measured. This process was repeated at different initial suspension concentrations. By plotting a
graph of the initial solid concentration ($C_o$) versus the ratio of sediment height ($h_s$) to initial suspension height ($h_o$), the first derivative of the function is the gel point [2].

Pure MFC-polymer sheets and two layer membranes comprised of the MFC-polymer on hardwood sheets were made using the Automatic British Handsheet Maker. Drainage time was measured as the time required for the water to completely drain forming a wet film on the filter mesh. Air permeability of the sheets was measured using the L&W Permeance tester. Dewatering force and water flux through the membrane as a function of polymer concentration was measured using compression load cell similar to the method described in Rainey et al. (2011) [3].

**Results and Discussion**

![Figure 1: (a) Gel point as a function of type of polymer and dosage (b) Fractional property change of dewatering pressure and pressure at a fix flux](image)

![Figure 2: Drainage time and porosity of MFC-polymer sheet as a function of gel point [2]](image)
Figure 1(a) shows that there are two distinct trends for the flocculation of CPAM and PEI with MFC. With an increasing dosage of CPAM, the gel point reduces reaches a minimum and then increases steadily. The addition of either PEI or CPAM to MFC reduced the gel point significantly until an addition level of 2 mg/g, after which, further addition of CPAM increased the gel point while further addition of PEI did not change the gel point. The minimum gel point achieved 0.08 kg/m³, compared to 0.24 kg/m³ without polymer addition. The difference in gel point trends observed are likely to be due to the different mechanisms by which the two types of polymers interact with nanocellulose fibres. Figure 1(b) shows that the independent variable controlling the behaviour of the MFC-polymer is the gel point. The lower the gel point, the less pressure is required to dewater the suspension and the lower the pressure required to achieve a given flux through the membrane. Figure 2 shows that a lower gel point corresponds to a faster drainage time. This is due to the more open floc structure that occurs with the addition of polymer. Reducing the gel point also increased the porosity of the sheet formed, suggesting that the more porous 3D structure of the flocculated MFC-polymer suspension is partially retained upon drying the 2D sheet.

**Conclusion**

It is evident that polymer addition to nanocellulose suspension is efficient at improving process ability and final nanocellulose film properties. A decrease in the gel point reduced the pressure required to dewater the MFC-polymer suspension at a given rate as well as reduce the drainage time required to form a sheet. This is due to the more open suspension structure which was also translated into a more open sheet with higher air permeability and porosity as well as a lower pressure to achieve a given water flux through the membrane.

**Acknowledgements**

The authors acknowledge financial support from the Australian Research Council, industries through the Industry Transformation Research Hub, Faculty of Engineering and Department of Chemical Engineering, Monash University.

**References**

Biography

Praveena Raj is an early career researcher who holds a Bachelor of Engineering (Chemical) degree, from Monash University, Australia. Praveena is in her final year of PhD at the Bioresource Processing Institute of Australia (BioPRIA) at Monash University. Her current research work is focused on studying the flocculation of polyelectrolytes with nanocellulose fibres for filtration and packaging applications.
COIL-STRETCH HYSTERESIS OF POLYMER SOLUTIONS AT FINITE CONCENTRATIONS
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Extended Abstract

Introduction

Nearly 40 years ago, de Gennes (Nobel Prize in Physics, 1991) predicted that polymer solutions could have different states of stress at the same strain rate, if their deformation histories were different. This phenomenon of “Coil-stretch hysteresis”, if true, would have significant impact on a variety of industrial applications involving polymer solutions, such as ink-jet printing and the spinning of nano-fibres. The existence of coil-stretch hysteresis was a highly debated topic for several decades within the rheology community, and there have been a number of theoretical and numerical investigations. However, in 2003, nearly 30 years after de Gennes’ hypothesis, the first experimental proof was obtained by Steven Chu’s (Nobel Prize in Physics, 1997) and Eric Shaqfeh’s groups at Stanford using stained DNA molecules undergoing elongational flow. Brownian Dynamics (BD) simulations supported these observations. All these studies, however, were carried out in the ultra-dilute limit, i.e., by observing the conformation (in the case of experiments) and performing simulations on single polymer molecules. From an industrial application perspective, on the other hand, polymer solutions are hardly likely to be in the ultra-dilute limit, but are more likely to be at finite concentrations. To the best of our knowledge, there are no prior simulations, or experimental investigations, on how concentration influences the extent of coil-stretch hysteresis exhibited in polymer solutions. In the context of numerical simulations, this is because there are two significant difficulties associated with simulating polymer solutions at finite concentrations. Firstly, one has to employ special periodic boundary conditions (PBC) that adapt to lattice deformation with the flow, so that, on the one hand they can mimic the infinite domain of polymer solutions, and on the other hand, enable simulations to be carried out for sufficiently long periods of time for attaining steady state results. Secondly, the simulations are excessively computationally intensive. In this study, a computationally efficient multi-chain Brownian Dynamics (BD) algorithm has been developed that enables the simulation of polymer solutions at finite concentrations experiencing planar shear flow, planar extensional flow, or planar mixed flow (which is a linear combination of planar shear and extensional flow), by implementing Lees-Edward PBCs for shear flows and Kraynik-Reinelt PBCs for mixed and extensional flows. We examine the non-monotonic influence of concentration on the extent of coil-stretch hysteresis. Our simulation results, which shown an increase followed by a decrease in coil-stretch hysteresis window size with increasing concentration, are supported by recent scaling arguments and experiments carried out by Prabhakar, Sridhar and Nguyen at Monash University. Moreover, de Gennes in his original theory predicted that in planar mixed flows, the coil-stretch hysteresis window would progressively decrease with increasing shear rate. We investigate the competitive influences of polymer concentration and flow mixedness...
on the extent of coil-stretch hysteresis in polymer solutions undergoing planar mixed flows, and map out the dependence of window size on concentration and shear rate.

**Numerical Solution Procedure**

A semidilute polymer solution is modelled as an ensemble of polymer chains represented by a linear bead-spring chain model, immersed in an incompressible Newtonian solvent. Each polymer chain is coarse-grained into a sequence of Nb beads that are connected by Ns (= Nb −1) massless springs that represent the entropic force between adjacent beads. In a cube of edge length L, a total of Nc chains are enclosed, resulting in a total of N = Nb × Nc beads per cell at a bulk monomer concentration of c = N/V, where V = L^3 is the volume of the simulation cell. The length scale and the time scale λ_H = ζ/4H are used to non-dimensionalize different equations. Here, H is the spring constant and ζ is the hydrodynamic friction coefficient associated with a bead. The Euler integration algorithm for the non-dimensional Ito stochastic differential equation governing the position vector r_v (t) of bead v at time t, is then given by:

\[ r_v(t + \Delta t) = r_v(t) + [\kappa \cdot r_v(t)] + \frac{\Delta t}{4} \sum_{\mu=1}^{N} [D_{\mu v}(t) \cdot F_{\mu v}(t)] + \frac{1}{\sqrt{\Delta t}} \sum_{\mu=1}^{N} [B_{\mu v}(t) \cdot \Delta W_{\mu v}(t)] \]  

(1)

\( \kappa \) is the velocity gradient tensor. The dimensionless diffusion tensor D_{\mu v} is a 3×3 matrix for a fixed pair of beads \( \mu \) and \( v \). It is related to the hydrodynamic interaction tensor, as discussed further subsequently. \( F_{\mu v} \) incorporates all the non-hydrodynamic forces on bead \( \mu \) due to all the other beads. The components of the Gaussian noise \( \Delta W_{\mu v} \) are obtained from a real-valued Gaussian distribution with zero mean and variance \( \Delta t \). The quantity \( B_{\mu v} \) is a non-dimensional tensor whose presence leads to multiplicative noise. The non-hydrodynamic force in the model is spring force \( F_{\mu v}^{\text{spr}} \).

A non-linear FENE (finite extensional non-linear elastic) spring potential is used here for modelling the spring forces.

**Results and Discussions**

![Figure 11a:](image)

Figure 11a: Dependence of concentration on the size of coil-stretch hysteresis window in pure planar elongational flow. The blue circles are results for initially stretched state and red circles are results for initially coiled state of the polymer chain.
Conclusions

This work addresses the phenomena of coil-stretch hysteresis in polymer solutions undergoing either pure planar extensional flow or mixed flow, i.e., a combination of shear and extensional flow, at finite concentrations. The study is carried out using a multi-chain Brownian dynamics (BD) algorithm which is capable of simulating polymer solutions at finite concentrations by successfully employing the appropriate periodic boundary conditions (PBCs). The present simulation result shows an increase in the coil-stretch hysteresis window size in pure extensional flow in agreement with the recent theoretical predictions by Prabhakar. Moreover, this study reveals that there is a competitive influence present between the concentration and flow mixedness parameter on the hysteresis window size in polymer solutions subjected to planar mixed flows.

References


Biography

Mr. Chandi Sasmal did his bachelors in Chemical Engineering from the Calcutta University followed by masters from the Indian Institute of Technology, Kanpur from the same discipline. Currently, he is a research scholar in the molecular rheology group of Monash University, and his research interest is to simulate the semi-dilute polymer solutions undergoing different kind of flows (shear, extensional or mixed) using Brownian dynamic simulations.
PLASMONIC NANO PARTICLE SYNTHESIS, FUNCTIONALIZATION AND SENSING APPLICATION

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1Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

Extended Abstract

Introduction

Building plasmonic structure particles has been a subject of increased interest over the past few years. Variety of morphologies and sizes of plasmonic structures have been synthesized [1, 2]. A fascinating aspect of plasmonic nanoparticles is that their optical properties that are strongly affected by structural parameters such as size and shape, as well as material composition and the surrounding dielectric environment [3, 4]. Synthesis of metallic nanoparticles with tailorable plasmonic signatures has been nourished by tremendous application and offered in many fields of materials and biomaterials science, including miniaturized optical devices [5] and electronic devices [6, 7], sensors [8] and photonic circuits [9], medical diagnostics and therapeutics [10, 11]. Although advances in strategies for synthesizing metal nanoparticles enabled control of size, shape and composition [12, 13], it is still a challenge to synthesis of desired nanostructure with controllable plasmonic property for advanced functional application.

One focus of this study is to fabricate new plasmonic gold building block. Here two novel plasmonic building blocks were fabricated, hairy gold nanorod and hairy gold bacteria. The length of gold nanowire can be tuneable. Due to the advantages of gold nanowire such as high flexibility and conductivity, hairy gold nanorod was applied in wearable sensor with enhanced performance in stretchability and durability.

In order to convert metal nanoparticles to more widely application, they typically need to be modified with some organic material that provides them with a desired functionality [2]. DNA-capped nanoparticles have demonstrated a plethora of exciting applications. Despite these advances, complex DNA corona structures remain elusive. The structures of DNA-capped nanoparticles, in particular their soft DNA corona, and the role of DNA in controlling interactions of DNA-coated nanoparticles were systematically investigated by combining small angle neutron and x-ray scattering with the data complemented by UV spectroscopy and dynamic light scattering.
The integration of nanoparticles to achieve the complex hierarchical macrostructures with multifunction is a key step for their practical applications. In these macromaterials, the nanoscale properties are preserved and new properties are generated as results of the interaction of their ordered constituents. Combination of bottom up and top down strategies to assembly nanoparticle into macrostructure is most promising route. In this study, gold nanoparticles were assembled into pyramid arrays by lithographic template. Hot points generated after assembly, in addition, the pyramid structure enhanced coupling effects, which is desirable efficient substrates for surface-enhanced Raman spectroscopy (SERS). The control over the nanocrystal shape allowed optimization of their performance for potential sensor applications.

Acknowledgements

This work is financially supported AINSE E06001 2437579 (GL 732041). This work was performed in part at the Melbourne Centre for Nanofabrication (MCN) in the Victorian Node of the Australian National Fabrication Facility (ANFF) and at Australian Nuclear Science and Technology Organisation (ANSTO).

References


Biography
Wenjuan Yang is a PhD student in the Department of Chemical Engineering at Monash University. Her research interests include design of plasmonic nanoparticles for applications in advanced materials, biology and sensor.
SIZE SEGREGATION OF PARTICLES DURING FILLING A PAUL-WURTH HOPPER

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Abstract

Granular materials are prone to segregate, driven by their various physical characteristics such as size, density, and shape. Segregation is often detrimental to subsequent processing where it can, for example, result in undesirable blend quality or handling problems. For an ironmaking blast furnace, burden materials (coke, sinter, pellets and fluxes) are weighed from bins in the stockhouse and delivered to the furnace top bins before discharged into the furnace by the burden distribution system. A typical ferrous batch may contain sinter, lump ore, pellets, limestone and small coke and represents a very wide range of sizes, shapes, and densities with the possibility to segregate at every handling step. Many studies have been carried out in the past decades on segregation phenomenon to develop understanding of the underlying mechanisms. However, most studies focus on the discharging process, and segregation during filling is less reported. To address this, size segregation of binary size mixtures of particles filling a blast furnace hopper is investigated using the discrete element method. The effect of different size ratios ranging from 1:2 to 1:8 and various volume fractions from 15% to 90% on segregation is examined. The results illustrate that, as size ratio increases, segregation becomes serious. But for size ratio above 4.0, the effect on segregation becomes less distinct. For volume fraction of small particles, segregation shows a parabolic trend and porosity reaches minimum value at around 30%-50%.

Biography

Tengfang Zhang is a PhD candidature in the Laboratory for Simulation and Modelling of Particulate Systems (SIMPAS), Department of Chemical Engineering, Monash University, VIC 3800 (email: tengfang.zhang@monash.edu). Her research focuses on segregation of granular materials in hopper flow. The main approach is discrete element method to simulate and analysis the microscopic parameters to quantify the flow process.
Biocompatible Gold Nanorods: Synthesis and Surface-modification

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Abstract
The most successful procedure for AuNRs synthesis was a seed-mediated method developed by El-Sayed et al. This method is relatively simple and economic, having a high yield (> 90%), and the produced gold nanorods are single crystals with a smooth morphology. However, this approach has several drawbacks: (1) reproducibility is less than ideal because this method requires strict experimental parameter control, e.g. NaBH₄ concentration, CTAB concentration, AgNO₃ concentration, quality of seed solution, pH and temperature, (2) laborious three-step protocol, and (3) its high sensitivity to the concentration of the reducing agent (ascorbic acid) leads to ionic-to-metallic gold conversion, which is only 15%. We developed a method to synthesize gold nanorods using simple seedless method and achieve 100% conversion of gold ions to metallic gold by creative protocol design, especially choosing appropriate reducing agents. And for nanorods surface modification, the conjugation of gold nanorods (AuNRs) with polyethylene glycol (PEG) is one of the most effective ways to reduce their cytotoxicity arising from the cetyltrimethylammonium bromide (CTAB) and silver ions used in their synthesis. However, typical PEGylation occurs only at the tips of the AuNRs, producing partially modified AuNRs. To address this issue, we have developed a novel, facile, one-step surface functionalization method that involves the use of Tween 20 to stabilize AuNRs, bis(p-sulfonatophenyl)phenylphosphine (BSPP) to activate the AuNR surface for the subsequent PEGylation, and NaCl to etch silver from the AuNRs. This method allows for the complete removal of the surface-bound CTAB and the most active surface silver from the AuNRs. The produced AuNRs showed far lower toxicity than other methods to PEGylate AuNRs, with no apparent toxicity when their concentration is lower than 5 μg/mL. Even at a high concentration of 80 μg/mL, their cell viability is still four times higher than that of the tip-modified AuNRs.

Biography

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2007 - 2011: Bachelor, School of Pharmacy, Shandong University, P.R.China
2011 - 2013: Master, School of Chemical and Bio Engineering, Gachon University, South Korea
2013 - 2015: PhD candidate (Prof. Justin Gooding), School of Chemistry, UNSW, Australia
2015 - Present: PhD candidate (Prof. Huanting Wang), School of Chemical Engineering, Monash, Australia
Post-synthetic Ti Exchanged UiO-66; enhancing the performance and industrial relevance of unsupported Metal Organic Framework Mixed Matrix Membranes

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Abstract

Membranes offer one of the lowest energy routes to carbon dioxide separation from flue gas. Key to handling the immense scale of Carbon Capture separations is achieving maximum membrane permeability while retaining sufficient selectivity for CO2 over N2. Mixed matrix membranes (MMM) offer an exciting potential to enhance separation performance over pure polymers, however also generate additional complications for optimizing their performance and feasibility for industrial implementation.

As we recently reported, metals can be post-synthetically exchanged in Metal-Organic Frameworks (MOFs) to drastically enhance gas transport performance in mixed matrix membranes. Ti-exchanged UiO-66 MOFs were found to triple CO2 gas permeability without a loss in selectivity. As a result, it is also shown that MOFs optimized in previous works for batch-wise adsorption applications can be applied to membranes, which have lower demands on material quantities. These Ti-exchanged membranes exhibit exceptional CO2 permeability enhancement of as much as 153% when compared to the non-exchanged UiO-66 mixed-matrix membrane controls, which places them well above the Robeson upper bound at 5 wt.% loading. Maximum permeability enhancement occurs at very low loadings, significantly less than the optimum for other MMMs, and is a major advantage for large-scale application due to the more attainable quantities of MOF required. Additionally, Ti exchange also had a significant effect in improving the mechanical properties of prepared films, exhibiting greater or higher mechanical stability over 3 months.

Biography

Stefan commenced PhD study in 2013 under the collaborative supervision of Associate Professor Bradley Ladewig, of Monash University (now Imperial College), and Dr Matthew Hill and Dr Cher Hon Lau of CSIRO. Stefan’s work centers on the development of super glassy polymer nanocomposite membranes, using MOFs and other porous frameworks. His research aims to tune the polymer-particle interaction to optimise separation performance, mechanical properties, and understand its effect on aging; key factors to the application of nanocomposite membranes to industrial processes. Recently, Stefan’s initial work on high performance Mixed Matrix Membranes containing Titanium exchanged Metal-Organic Frameworks was published by Scientific Reports.