Rheological behaviour of Na-CMC and Na-alginate as binders for lithium ion batteries.

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DECLARATION

The work presented in this thesis is the original work of the author under the supervision of Dr James J. Leahy & Dr Maurice Collins. Other sources of information, when used, have been acknowledged. No part of this thesis has been submitted to this or any other university.

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Abstract

Lithium ion batteries are the current technology of choice for electric vehicles due to their light weight, high volumetric and gravimetric energy density, low self-discharge rate, quick charge acceptance, excellent cycle life and wide operating temperature range. However the current manufacturing process requires the use of polyvinylidene fluoride (PVDF), in order to bind the anode components within the electrode which prevents the recycling of the electrode materials. Furthermore PVDF necessitate the application of N-methyl-2-pyrrolidone (NMP), an environmentally toxic material as a solvent during the manufacturing. The aim of this research was to investigate the suitability of using water soluble Na-alginate as an alternative binder for the anodes of lithium ion batteries to reduce the environmental impact from current manufacturing processes and to allow recycling of the active anode components. The main function of the binder is the improvement of the mechanical strength and the adhesion of the electrode on the current collector. The properties of the binder which are most important during manufacturing are the rheological characteristics of the slurries comprising binder and active materials. This was the focus of this investigation.

The viscosity of Na-alginate suspensions at 1% or 1.5% loading in water were typically 1 to 8 Pa·s which are similar to PVDF suspensions with loadings of 2.5 to 3.0%. Comparing to the benchmark Na-CMC, the degree of flocculation shows that for the same concentration of binder in water, Na-alginate suspensions are more stable, Na-alginate has a degree of flocculation of 1.17 while for Na-CMC it was 1.90. The rheology measurements show that Na-alginate slurries have a higher viscosity than Na-CMC at a shear rate of 50 s⁻¹ with that for a 1.5% of Na-alginate binder being 1.26 Pa·s while for Na-CMC it was for 0.20 Pa·s. The loss factor was lower for Na-alginate, between 2 and 3 against between 2.9 and 3.3 for Na-CMC, showing a more developed network structure.

The casting and drying process, demonstrated that while 1.5% Na-CMC in water wasn´t sufficiently viscous to cast the slurries it was possible to do it with Na-alginate
Table of contents

1. Introduction ............................................................................................................. 2
   1.1. History of power storage devices ................................................................. 2
   1.2. Lithium ion batteries .................................................................................... 4
       1.2.1. How they work .................................................................................... 5
   1.3. Materials .......................................................................................................... 6
       1.3.1. Binder ..................................................................................................... 7
       1.3.2. Conductive additive and active material ................................................. 9
   1.4. Disadvantages and risks of PVDF ................................................................. 10
   1.5. Aim of the research ....................................................................................... 11
   1.6. Why Na-alginate and Na-CMC? ................................................................. 11
   1.7. The Greenlion Project ................................................................................. 12

2. Methodology ........................................................................................................ 18
   2.1. Material content and mixing methods .......................................................... 18
       2.1.1. Material content ................................................................................... 18
       2.1.2. Mixing Methods .................................................................................... 19
   2.2. Degree of flocculation .................................................................................. 20
   2.3. Rheology .......................................................................................................... 22
       2.3.1. Classification of flow behaviour .............................................................. 22
       2.3.2. Interactions between suspended particles in suspensions ................. 23
       2.3.3. Rheology of slurries .............................................................................. 26
       2.3.4. Definitions and measurements ............................................................... 31
   2.4. TGA ............................................................................................................... 35
2.5. Casting onto current collector ................................................................. 37

2.6. SEM .................................................................................................. 37

3. Results and discussion ........................................................................... 39
   3.1. Degree of flocculation ................................................................. 39
   3.2. Rheology ..................................................................................... 45
      3.2.1. Viscosity and shear stress .................................................. 45
      3.2.2. Loss Factor (Tanδ), Loss Modulus and Storage Modulus ..... 55
   3.3. TGA ............................................................................................ 64
   3.4. SEM ............................................................................................ 68

4. Conclusions ........................................................................................ 75

5. References .......................................................................................... 77
CHAPTER 1

INTRODUCTION
1. Introduction

1.1. History of power storage devices

Alessandro Volta was the inventor of the first battery (1800). It was made of disks of copper and zinc separated one from the other by cardboard disks moistened with water and salt or acid as it can be seen in Figure 1.1. From that battery Daniel (1836) created a cell composed of two electrolytes. After that Leclanche (1866) created a cell using zinc as cathode and carbon as anode.

![Volta’s battery](image)

**Figure 1.1 Volta’s battery**

In 1898 the Columbia (Figure 1.2) was the first commercially available battery. It was a 1.8 volt, carbon-zinc battery with an acidic electrolyte. It became the basis for every dry cell battery for next sixty years[1].
The chemistry of batteries has changed over the years and there is now a wide range of batteries available depending on the size, current, capacity and materials used.

In 1859, Gaston Planté a French physician invented the first rechargeable battery which was based on lead acid and is a system that is still used nowadays.

$$8\text{MnO}_2 + 4\text{Zn} + \text{ZnCl}_2 + 9\text{H}_2\text{O} \rightarrow 8\text{MnOOH} + \text{ZnCl}_2 \cdot 4\text{ZnO}.5\text{H}_2\text{O}$$

**Figure 1.2** Schematic of the Columbia dry cell battery

**Figure 1.3** Different types of batteries

In 1859, Gaston Planté a French physician invented the first rechargeable battery which was based on lead acid and is a system that is still used nowadays.

$$\text{Pb}^+ + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + \text{H}^+ + 2\text{e}^-$$

$$\text{PbO}_2 + 3\text{H}^+ + \text{HSO}_4^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$$

$$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$$
In 1899, Waldmar Jungner invented the nickel-cadmium battery (NiCd), in which the positive electrode (cathode) was nickel and cadmium was the negative (anode). The high cost of the materials compared to the lead acid battery limited its use.

However in 1901, Thomas Edison replaced cadmium with iron which reduced the cost but the battery had low specific energy, poor performance at low temperature and high self-discharge so that limited the success of the nickel-iron battery. Then in 1932, Shlecht and Ackermann invented the sintered pole plate achieving higher load currents and improving the longevity of NiCd. In 1947, Georg Neumann succeeded in sealing the cell. NiCd was the only rechargeable battery for portable applications until in the 1990s, environmentalists in Europe became concerned about environmental contamination arising from the disposal of NiCd. This was the catalyst for the consumers to switch to Nickel-metal-hydride (NiMH), a more environmentally friendly battery (NiMH were the first batteries used in the first generation of hybrid electric cars) which are being now supplanted by lithium-ion batteries.

1.2. Lithium ion batteries

Since SONY manufactured the first commercial lithium ion battery in the 90s, extensive research and efforts have been done to improve the battery performance and to reduce the costs. These research efforts have mainly focused on two areas, electrochemistry and materials processing. Some research is focused on the improvement of the reaction by investigating new materials while other research is focused on how the batteries are manufactured[2, 3].

As it can be seen in Figure 1.4 lithium offers a higher energy density with a higher energy density.

The environmental protection and recyclability are other issues of concern regarding the manufacturing of Li-ion batteries. This is the key driver of recent research to investigate new environmentally friendly materials that can replace those that are being used now[4].
1.2.1. How they work

The most common battery consists of a cathode made of a lithium metal oxide (e.g. lithium cobalt oxide) on a copper collector, a graphite anode on an aluminium collector and an electrolyte consisting of a lithium salt (e.g. LiPF$_6$) dissolved in an organic solvent such as ethylene carbonate - dimethyl carbonate (EC-DMC).

$$yC + LiMO_2 \leftrightarrow Li_xC_y + Li_{(1-x)}MO_2 \quad x \sim 0.5, \; y = 6, \; \text{voltage} \sim 3.7V$$

The electrochemical process inside the battery, as the previous equation shows, involves the reversible extraction and insertion of lithium ions between the two electrodes through the electrolyte with the removal and addition of electrons [5, 6]. This is an intercalation reaction in which ions or molecules are reversibly inserted into a crystalline lattice without any significant change of that lattice [7]. LiCoO$_2$
batteries taken as an example (see Figure 1.5), in which the overall reaction is as follows:

\[ \text{C} + \text{LiCoO}_2 \leftrightarrow \text{LiC}_6 + \text{Li}_{0.5}\text{CoO}_2 \]

More specifically in the cathode, when discharging, electrons are removed towards the anode through the electrolyte by removing a Li ion from LiCoO\(_2\) as the following reaction shows:

\[ \text{LiCoO}_2 - \text{Li}^+ - e^- \leftrightarrow \text{Li}_{0.5}\text{CoO}_2 \Rightarrow 143 \text{ mAh/g} \]

While at the anode the lithium ions are bonded to the carbon by the addition of electrons as the following equation shows:

\[ 6\text{C} + \text{Li}^+ + e^- \leftrightarrow \text{LiC}_6 \Rightarrow 372 \text{ mAh/g} \]

![Figure 1.5 Schematic of a Lithium Ion battery](image)

1.3. Materials

As commented before, the main components of the battery are the electrodes and the electrolyte. The electrodes can be positive or negative and inside those three
different components can be found, an active material, a conductive additive and a binder.

During manufacture these three materials are normally mixed using a solvent and then coated and dried onto the current collector. Depending on the type of solvent used the suspension can be classified as either a water-based system or an organic solvent-based system[8].

The anode in a Lithium ion battery normally consists of three different materials: an active material, a conductive additive and a binder.

1.3.1. Binder

The binder is the material that keeps everything together, it must bind the active material and conductive additive together and to the current collector, it should be chemically and electrochemically stable and has to allow the incorporation in water of the hydrophobic carbon black. Also, it has to have proper rheological properties when used in the slurry in order to cast the slurry onto the current collector[9]. Currently, the most widely used binder is polyvinylidene fluoride (PVDF) with N-methyl-2-pyrrolidone (NMP) used as a solvent. [2, 10, 11]. In this research the behaviour of the Na-alginate and Na-CMC as binding materials were studied.

1.3.1.1. Na-alginate

Sodium alginate is the salt of alginic acid, which is extracted from all varieties of brown algae. It is a water soluble polysaccharide biopolymer consisting of two uronic acids: β-L-Mannuronic and α-L-Guluronic acid. Depending on how they bond the blocks can be described as GG blocks (Guluronic-Guluronic), MM blocks (Mannuronic-Mannuronic) and MG blocks (alternating bonding). The rigidity of the chains decrease with different bonding options as follows: GG > MM > MG, consequently, properties, such as viscosity depend on the ratio of G and M blocks as it can be seen in Figure 1.6 [12-15]. Na-alginate is widely used as a thickening, film
forming, emulsifying and gelling agent in the food industry and for drug delivery in the pharmaceutical industry[16].

The Na-alginate used in this research was obtained from Sigma-Aldrich and was categorized as medium viscosity which according to the manufacturer's specifications, a 2% w/v solution has a viscosity of approximately 2.0 Pa-s at 25°C.

1.3.1.2. Na-CMC

Na-CMC is a linear polymeric derivative of cellulose, consisting of linked glucopyranose residues with varying levels of carboxymethyl substitution (Figure 1.7). It is water soluble due to the addition of the carboxymethyl groups which can be substituted up to a substitution degree of 3[10, 17].

![Figure 1.6 Representation of a Na-alginate chain and the different bonding options.](image)

![Figure 1.7 Representation of a Na-CMC molecule.](image)
The Na-CMC used in this research was obtained from Sigma Aldrich. It has an average molecular weight of 250,000 Da and a degree of substitution between 0.65 and 0.90. According to the manufacturer’s specifications, a 2% w/v solution has a viscosity of approximately 0.4-0.8 Pa•s at 25°C.

1.3.2. Conductive additive and active material

The active material is the material that exchanges the lithium ions and the electrons. In the cathode the active material is the lithium metal oxide whilst in the anode graphite is the major material used[2].

Lithium is the most electropositive and the lightest of all metals[3] with a high voltage, high volumetric and gravimetric energy density, low self-discharge rate, no memory effect, quick charge acceptance, excellent cycle life and wide operating temperature range[18].

Graphite has an excellent cycling behaviour with a reversible capacity of 372 mAh/g and it is stable with the Li metal. It can sustain at least 800-1000 cycles but its electrochemical performance in the anode depends on the crystalline make up, furnace processing atmosphere and maximum heat-treatment temperature[2, 19].

The conductive additive is added to improve the conductivity between the active particles. Carbon black is the most commonly used material in both electrodes and it gives a larger first-cycle irreversible capacity and a low charge/discharge capacity[20-22].

In this research, both the conductive additive and active material were obtained from TIMCAL, a partner in the Greenlion project who has been developing these materials specifically for lithium ion battery applications.

Carbon black “Super C45” was used as the conductive material, referring to it’s reported specific surface area (BET) of 45 m²/g. “Super C”’s were specifically developed for mobile energy applications, and have reportedly improved control of material purity which is a key requirement for battery mass production.
The active material is graphite “TIMREX SLP30” a “potato-shape” graphite shown in Figure 1.8. It has a particle size (d90) of 32 µm and a specific surface area (BET) of 7 m²/g [23].

![Figure 1.8 SEM micrograph of a TIMCAL graphite especially optimized for use as the negative electrode material](image)

1.4. Disadvantages and risks of PVDF

The greatest disadvantage of using PVDF as binder in lithium ion batteries is the need for an organic solvent such as the NMP. This solvent is flammable and environmentally unfriendly. It is also mutagen, tumorigenic and a reproductive effector. Because of this, when the slurry is dried, the solvent has to be collected and purified for reuse which increases the cost of processing. The PVDF itself is expensive (Sigma Aldrich 430€ for 250 g) and it is not easy to recycle due to its flammability and toxicity [2, 4, 9, 10, 24, 25].

An additional disadvantage is that the PVDF can react with the active materials in the electrodes at high temperatures creating a self-heating thermal runaway which may lead to explosion of the battery [10, 25].
1.5. Aim of the research

As part of the Greenlion project the research reported in this thesis focused on investigating the suitability of Na-alginate and Na-CMC as binders and more specifically in terms of the electrode processing.

In order to achieve this objective, rheological properties such as viscosity, shear-stress and loss and storage modulus will be analysed along with the degree of flocculation and thermogravimetric analysis to understand the behaviour of these materials during this thermal curing process.

Finally, in order to see the structure of the final product, SEM images were used.

1.6. Why Na-alginate and Na-CMC?

Some researchers have already suggested Na-CMC as a possible binder for lithium ion batteries.

Mancini et al. (2011) demonstrated the suitability of the Na-CMC as binder for an anatase TiO$_2$ anode. They suggested such anodes provide greater compactness and better electrochemical behaviour than anodes made with PVDF[10].

Kim et al. (2011) measured the performance of a lithium ion battery containing CMC as binder both for cathode and anode, using an electrolytic solution based on ionic liquids and they found that the use of Na-CMC reduces the need for post-coating treatment and makes easier the disposability of the battery at the end of its life[24].

Jeong et al (2012) suggested that the properties of electrodes made with natural cellulose were similar to those made from PVDF[11]. Courtel et al (2011) demonstrated that the replacement of the PVDF by water soluble binders like the Na-CMC is possible[25].
Cuesta et al. (2015) demonstrated the viability of the Na-CMC and Na-alginate among other hydrocolloids. The showed that the electrochemical performance of the electrodes made with these two binders was comparable to the PVDF[26].

Lee et al. (2005) investigated the effect of the degree of substitution of CMC on its dispersion properties. They found that a CMC with a lower degree of substitution has a more hydrophobic nature and therefore enhances its interaction with graphite[17].

It was decided to use Na-CMC as a benchmark for comparison with the Na-alginate and to test it as well with the other material components that were being investigated in the Greenlion project such as the Graphite SLP30 and the Carbon Black Super C45.

The fact of the two materials being water soluble is the main reason for why they were chosen for this research. That allows Greenlion to avoid the toxic solvents used with the PVDF. The alginate and CMC are environmentally friendly and it is easier to recover the active and conductive materials by pyrolysis of the binder [4, 10, 11, 24].

The price of these binders compared to the price of the PVDF is a good reason as well. As an example of this the prices of each materials at Sigma Aldrich are as follows: PVDF 430€ per 250 g, Na-CMC between 119€ and 353€ per kg and Na-alginate between 109€ and 411€ per kg.

1.7. The Greenlion Project

GREENLION was a large scale collaborative project funded under the European Commission FP7 program with the goal of manufacturing greener and cheaper Li-Ion batteries for electric vehicle applications via the use of water soluble, fluorine-free, high thermally stable binders, which would eliminate the use of volatile organic solvents and reduce the cell assembly cost.
GREENLION had 6 key objectives:

- development of new active and inactive battery materials viable for water processing, i.e. not use any toxic solvent. (green chemistry)
- innovative processes (coating from aqueous slurries) leading to reduced electrode production cost and environmental pollution
- development of new assembly procedures (including laser cutting and high temperature pre-treatment) capable of substantially reduce the time and cost of cell fabrication
- lighter battery modules with air cooling and easier disassembly through eco-designed bonding techniques
- development of an automated module and battery pack assembly line for increased production output and reduced cost
- waste reduction, which, by making use of the water solubility of the binder, allows the recovery of the active and inactive battery materials
The goal was to improve the competitiveness of European battery producers compared to their Asian counterparts through the development of new chemistry/technologies based on innovative materials and processes in this manufacturing value chain, allowing for:

1. the more environmentally friendly production of the battery components;
2. the substantial shortening of the battery assembly procedure, and
3. the easier and more effective disassembly and end-of-life recycling.

Altogether, these improvements will allow higher energy efficiency and substantial production cost reductions thus ensuring a real competitiveness based on new technological IP rather than only mass production optimization.

In the GREENLION project, we addressed these issues by the industrial development of eco-designed processes at the electrode, cell and battery module level. At the electrode processing stage (that will be otherwise independent of the active materials chemistry), developing and making use of:

1. aqueous slurries rather than toxic organic volatile compounds
2. non-thermoplastic polymers that allow for high temperature drying, which results in shorter and less expensive assembly procedure and 
3. easily disposable non-fluorinated polymers.

At the cell assembly level, further improvements to the existing procedures as well as changes at some steps of the assembly process will be developed to increase energy efficiency and shorten times (and hence lower costs) during the manufacturing process, by implementing:

1. laser cutting instead of mechanical notching of the electrodes,
2. adjusted stack winding of components from aqueous-based electrodes and their drying process before electrolyte filling and sealing, to lower dry room requirements,
3. environmentally friendly bonding process for more effective and long-life cell sealing, and
4. adjusted formation step time (ideally for electrodes with reduced formation cycle) in cell manufacturing line (5% time reduction).

Finally, developing a modular battery allows an easier handling of cells within a complete battery pack. At this battery module level, GREENLION project designed an autonomous prototype unit including its own electrical and thermal management as a simple and reliable building block that will allow the manufacturing and maintenance of the whole battery packs easier and more inexpensively, with the lowest possible environmental impact. This was achieved by:

1. lighter battery module designs (including electronics) by implementing air cooled solutions instead of liquid cooling systems (expected 20% less weight),
2. bonding process of module housing for safe operation but easy disassembling for maintenance and reuse/recycling at their end-of-life, and
3. automation of module assembly process (3 seconds per cell vs. manual assembly).

These developments were scaled-up and realized in pilot lines during the project, following a continuous environmental assessment of materials and processes. A validation of the finally assembled battery module was carried out lead by SEAT, the automotive end-user, who provided the targets and specifications for electric vehicles application.
CHAPTER 2

METHODOLOGY
2. Methodology

2.1. Material content and mixing methods

2.1.1. Material content

In order to investigate the behaviour of the two selected materials as binders for the anode, it was decided to work with different concentrations and different ratios of each material. Two main variables were chosen, w/w concentration of the binder in water and the mass ratio of the three materials within the dry matter of the slurry. This last variable referred to here as X/Y/Z where X is the binder, Y is the conductive additive and Z is the active material.

The suspensions and slurries were prepared as follows:

- Initially the binder was weighed to make a 1% or 1.5% w/w suspension.
- The water was added.
- Assuming that the amount of binder in the suspension was 5% dry matter, the required mass of carbon black and graphite, were calculated and added.

![Figure 2.1 Example of three different suspensions with their real and assumed dry matter percentage](image-url)
2.1.2. Mixing Methods

Some researchers suggest that the order of mixing of components of the slurry can have an effect on its rheological properties. Kim et al. (2011) used four different methods where the first method consisted of adding the conductive material and the binder simultaneously and placing them under vacuum. After that the active material and liquid solvent where added and slurry was stirred for 30 minutes. Method 2 was as method 1 but the addition of conductive and active materials were interchanged. Method 3 all the materials were added simultaneously and placed under vacuum and in method 4 the conductive and active materials were initially mixed under a dry atmosphere and after that the binder solution was added and stirred. They found that there were differences in viscosity over time due to the different particle sizes and shapes and that method 4 gives the highest level of liquid absorption and the best dispersion state.[27]

Li et al. (2012), also, tested two different mixing methods consisting on the first method being mixed everything together except for the second binder. After 1 day mixing they added the second binder and mixed for another 3 days. The second method consisted of mixing everything together for 4 days. They found that the agglomeration of the powders was lower in method 1. Also the dispersion of the slurry was better in method 1. They suggest that the adsorption priorities of the organic additives could be the reason[28]

It was decided to test if the mixing procedure would have an effect on the final slurry therefore 2 different methods were chosen. Due to one of the aims of the project being to minimise cost, the selected methods had to be simple and not involve the addition of extra materials or equipment that would increase the final cost of the production.

As Figure 2.2 shows, method one consists of mixing the water, the binder and the conductive additive first for 24 hours. Subsequently the active material was added and mixing was continued for another 24 hours. Method two consisted of mixing all components together from the beginning for 48 hours (to make the total time the same in both methods).
Slurries were prepared in a ball mill using cylindrical zirconium rods 10mm in length with a diameter of 5mm in order to avoid agglomerates[8]. For that, all the components of the slurry were weighted in a 50 ml plastic container, then, the needed amount of water was added. After that, one and a half times the weight of the slurry in zirconium rods was added. The mixing process was done in an horizontal ball mill at a speed of 200 rpm.

Figure 2.2 Schematics of the 2 different methods used.

2.2. Degree of flocculation

Flocculation is the process in which the particles suspended in a liquid medium, form larger aggregates known as flocs. The formation of these flocs depends on the balance of electrostatic interactions i.e., the chemistry of the dispersions and the repulsive and attractive forces between particles [29]. When they are formed, and due
to the difference in density between the aggregates and suspending medium, bigger flocs settle faster and generally accumulate at the lowest position in the suspension. Once equilibrium is reached a sharp interface can be observed between the settled flocs and the remainder of the suspension.

The degree of flocculation (\( \beta \)) is the ratio of the sedimentation volume of the flocculated suspension \( F \), to the sedimentation volume of the deflocculated suspension, \( F_Y \).

\[
\beta = \frac{F}{F_Y}
\]

Or

\[
\beta = \frac{\frac{V_U}{V_0} (Flocculated)}{\frac{V_U}{V_0} (Deflocculated)}
\]

Where \( V_U \) is the volume of the sediments and \( V_0 \) is the total volume of the suspension. In this case, because the total volume doesn't change:

\[
\beta = \frac{V_U (Flocculated)}{V_U (Deflocculated)}
\]

The degree of flocculation over a fixed time period, (7 days in the case of the experiments reported here), can be used as an indicator of the suspension’s stability. Closer to 1 the value of \( \beta \), i.e. larger the volume of the settled flocs, means that more time is needed for the flocs to completely settle and separate into 2 different phases.

An understanding of this phenomenon is important for battery production particularly in the preparation of the anode slurries and their subsequent pumping, coating and drying. For proper homogenization of the three component materials once the slurry is dried, it has to be stable and avoid any settling or separation during
the time needed for the anode production [28, 30]. Alternatively, the time needed for the whole process can be adjusted to the time that the slurry needs for deflocculation.

In order to measure the degree of flocculation, the samples were placed in graduated cylinders over a period of 7 days, and volume of each phase was noted.

2.3. Rheology

There are a large number and range of variables encountered in suspensions or slurries of solid particles in liquid media which cause the flow behaviour of these systems to vary. A range of different approaches and methods of analysis are necessary to describe their behaviour in various flow regimes. The variables that have a major influence on the hydrodynamics of these systems include solids loadings (i.e. volume fraction), particle size, particle size distribution, particle shape, active surface area, additives, pH and flow regime. There are also factors that influence the degree of particle-particle or fluid-particle interactions such as the degree of wettability of the solids, surface charge of the particles and the ionic nature of the liquid. These latter factors can be strongly influenced and controlled (to a degree) by inclusion of various additives such as surfactants, polymers, and ionic species such as acids, bases and salts [31].

2.3.1. Classification of flow behaviour.

It is widely recognised that the flow behaviour of slurries and suspensions can be classified into three or more general categories. Since there are obviously no sharp boundaries between these categories, a number of sub-categories are also possible. These three broad categories are homogeneous, heterogeneous and saltation flow behaviour [31]. In homogeneous flow, the solids loading is relatively high and the particles are much smaller than the dimensions of the conduit and are sufficiently uniformly dispersed so that the mixture can be treated as the equivalent of a uniform single-phase liquid.
The mixture can be considered heterogeneous if the particles are sufficiently large, dense and in a dilute state so that settling will occur to various degrees and the particles will be no longer be uniformly distributed over the flow field. The majority of the particles may be still in suspension if there is sufficient mixing or agitation. The analysis of the flow behaviour in this situation must consider separately the forces on the particle resulting from the interaction with the surrounding suspending medium.

At some point, the larger and/or denser particles will settle to the bottom of the conduit and form a bed, which constitutes a saltation regime. The particles in the bed will tend to form “dunes” and will move or slide along the bottom of the conduit if the shear forces due to the moving fluid are large enough. If not, the bulk of the bed may be stationary but particles on the surface may be swept along in a bouncing-type of motion.

Many flows may be clearly homogeneous or heterogeneous but a considerable number of flow regimes are a combination of both. This is because the single most important parameter that governs the flow regime and hence the rheology is the particle size. Suspensions of very fine particles most often exhibit homogenous flow behaviour whereas slurries of coarse particles are generally heterogeneous. However, systems with a rather broad particle size distribution are often encountered, and indeed are often desired for optimum flow behaviour [31]

2.3.2. Interactions between suspended particles in suspensions.

There is a range of interactions between particles in suspension, including hydrophobic, hydrophilic, attraction and repulsion.

Water is an unusual substance when dealing with intermolecular forces [32]. There are two types of interaction, the hydrogen bond and the hydrophobic effect. The hydrophobic effect occurs when water molecules come in contact with for example hydrocarbon molecules. When the water molecules come in contact with such a molecule, they are faced with an apparent dilemma, in the direction the water molecules face. It would appear that one or more of the four charges per molecule
will have to point towards the inert solute molecule and be lost to hydrogen bond formation. Clearly, the optimum configuration will have the least number of tetrahedral charges pointing towards the unaccommodating species so that the other charges can point towards the water phase and so be able to participate in hydrogen bond attachments. If the non-polar solute molecules are not too large, it is possible for water molecules to pack around the solute without giving up any of the hydrogen bonding sites. Examples of such an arrangement are the dispersion interaction between water and hydrocarbons. This is not very different from that between water or between hydrocarbon and hydrocarbon so that the main effect of bringing water molecules and non-polar molecules together is the reorientation of the water molecules. This reorientation allows water molecules to participate in hydrogen bond formations more or less as in bulk water.

Indeed, since water molecules in the liquid state participate in an average of approximately 3-3.5 hydrogen bonds, it would appear that around an inert solute molecule, the water molecules actually have a higher co-ordination of 4 and thus be even more ordered than in the bulk liquid. It is also clear that the sizes and shapes of the non-polar (hydrophobic) solute molecules are critical in determining the water structure adopted around them. This is often referred to as hydrophobic solvation or hydrophobic hydration.

2.3.2.1. Hydrophilic interactions

In hydrogen bonding, it is a straight forward matter to ascertain which bond is responsible for the hydrophilic interaction [32]. The intermolecular hydroxyl group is used based on the bond distance and this bond has some covalent character. While there is no phenomenon known as the hydrophilic effect, such effects can be recognised in the propensity of certain molecules and functional groups to be water soluble and repel each other strongly in water. Hydrophilic groups prefer to be in contact with water than with each other. As might be expected, strongly hydrated ions are hydrophilic, but some uncharged and even non-polar molecules can be hydrophilic if they have the right geometry and if they contain electronegative atoms capable of associating with the hydrogen bond network in water.
2.3.2.2. Attraction

When the interface between solid suspended particles and the surrounding liquid is stable, the interface gives a positive contribution to the Gibbs free energy [31]. A decrease of this interface between the solid and liquid leads to a reduction in the Gibbs free energy and such processes are thermodynamically possible at constant temperature and pressure. One of these processes is aggregate formation.

On a molecular level the tendency towards aggregate formation is caused by the fact that the London-Van der Waals attraction between similar particles is larger than between dissimilar particles, causing a potential energy decrease when two particles approach each other. The attractive energy is independent of the size of particle but the resultant force decreases with increasing particle size:

\[
\frac{\delta V_a}{\delta r} = \frac{1}{a} \left( \frac{\delta V_a}{\delta s} \right)
\]

where: “r” is distance between centres of the particles, “a” is the particle radius, “s = r/a” and “\(V_a\)” is the force of attraction.

Hydrodynamic friction forces, on the other hand, increase with increasing particle size, thus the attraction will become more pronounced for smaller particles.

2.3.2.3. Repulsion

The fact that all suspensions are not prone to aggregate formation is due to two main types of repulsion which retard coagulation to such an extent as to prevent it. Electrostatic repulsion is caused by the presence of electrical charges on the surface of the suspended particles in a polar medium. This surface charge arises because of
differences in absorption or dissolution tendencies between different ions. The whole system is electrically neutral, thus there is a counter ion charge, equal but opposite in sign to the surface charge. The counter ions are distributed like an atmosphere around the particle. The surface charge causes a potential difference in the liquid between the points very close to the surface and points in the bulk liquid, thus in turn causing a repulsion between two particles carrying surfaces of the same sign.

The other main type of repulsion occurs when the surfaces of the suspended particles are covered by adsorbed macromolecules resulting in steric repulsion. This is determined mainly by the quality of the dispersion medium as a solvent for the adsorbed polymers. If present in small amounts only, steric stabilising agents can act as flocculating agents because polymer molecules may be adsorbed on two different particles and act as bridges. Aggregate formation is generally indicated by shear thinning behaviour and a time dependence which can be expressed as aggregate degradation by shear over time [31].

2.3.3. Rheology of slurries

Rheology is the science of the deformation and flow of matter. It is the branch of physics concerned with the mechanics of deformable bodies. Much of the theory of rheology deals with idealised cases modelled using first-order differential equations and on the concept that the constants in these equations do not vary with changes in the recognised variables [33]. However there are numerous exceptions to the ideal models which have been developed mathematically.

Typically a rheological experiment comprises the study of the relationship between the deformation rate (or shear rate), \( \gamma \), and the shear stress, \( \tau \), where \( \tau \) is the force per unit area necessary for maintaining the shear rate concerned. This ratio of shear stress to shear rate is called the Newtonian viscosity for Newtonian fluids or the apparent viscosity for non-Newtonian fluids. Frequently the rheological behaviour depends also on time, \( t \), during which a shear rate is maintained.
2.3.3.1. Classification of fluid behaviour

There are two main classes of fluid behaviour, Newtonian and non-Newtonian fluids. In the case Newtonian fluids for a liquid under shear, the rate of deformation or shear rate is proportional to the shearing stress. A typical rheogram is presented in Figure 2.3.

Non-Newtonian fluids are characterised by measuring apparent viscosity or shear-stress at a number of different shear rates with a rotational viscometer. Typical flow curves for non-Newtonian fluids are presented in Figure 2.3.

![Flow curves for various ideal rheological models](image)

**Figure 2.3** Flow curves for various ideal rheological models

When the rate of shear stress decreases more than in proportion to the shearing rate, the material is called a pseudo plastic or shear thinning liquid. To a first approximation, the flow curve of a pseudo plastic liquid can be represented by a power law mathematical expression, i.e. the rate of shear is roughly proportional to the power of the shearing stress or vice versa.

A material exhibiting a flow, where the rate of shear stress increases more than in proportion to the shearing rate is called a dilatant or shear thickening fluid. The shape of their flow curves can also be roughly approximated by a power function. In
other words, to a first approximation, pseudoplastic and dilatant fluids give straight lines when the log of shear rate is plotted against the log of shear stress.

In cases in which the shear stress is proportional to shear rate with a yield value, these materials are called Bingham plastic fluids. These fluids exhibit Newtonian behaviour with a yield value. Certain materials which flow readily if a shear rate is applied will not flow at all if the shear rate is reduced below a certain value called the yield value[34]. Examples of this type of behaviour are well known, being evidenced by such diverse materials as cake frosting, beaten egg white, putty, and raw ceramic clay ready for turning on a potter’s wheel. Once the yield value has been exceeded, the rate of shear is proportional to the shear stress, as in the case with Newtonian liquids. A fluid exhibiting this type of behaviour is called a plastic substance or a Bingham body.

The two bodies exhibiting non-linear flow at stresses exceeding the yield value are called pseudoplastic fluid with a yield value and a dilatant fluid with a yield value.

The presence of a yield value introduces experimental difficulties in flow measurements for all geometries in which the rate of shear is not uniform throughout the body of the fluid. The five curves shown in Figure 2.3 refer to equilibrium effects and should be considered independent of time. However, it is found that many fluids exhibit time dependent flow effects, which can either be spontaneously reversible or irreversible. With respect to reversible behaviour, certain materials are found to become more fluid with increasing time of flow under steady-state conditions, such materials are said to exhibit thixotropy. The opposite reversible effects, in which the material exhibits more resistance to flow with increasing time while being subjected to steady-state shear, is called rheopexy [33].

2.3.3.2. Rheological models

The rheological data may be utilised directly for characterising a given fluid or suspension or for predicting flow behaviour under certain conditions. However, it is more convenient and more useful if the data can be represented by an appropriate
equation or model. Also, it is desirable to have a model which is as mathematically simple as possible and yet adequately represents the important characteristics of the material. A wide variety of models have been proposed for representing the viscosity function for suspensions of varying degrees of complexity. Although there is some degree of logical deduction behind some of the models, they are largely empirical curve-fit equations for representing data. The more complex models are capable of representing more complex behaviour although they are also more difficult to evaluate and to apply and often are not necessarily more useful in a practical sense [31].

Four models which have been useful for representing suspension viscous properties are shown in Table 1. Each model is written in three different but equivalent forms. These models are relatively simple in that only two or three parameters are needed to determine the viscosity function. Certain characteristics of these models should be noted. The Power Law or Ostwald-de Waele model contains two parameters, the flow index, \( n \), and the consistency coefficient, \( m \). It can represent Newtonian \( (n = 1) \), shear thinning \( (n < 1) \), or shear thickening \( (n > 1) \) behaviour and \( m \) is the value of the apparent viscosity at a shear rate of one reciprocal second. Although most materials exhibit a “power law” region over a shear rate of up to two decades, the model will fail at very high and or low shear rates.

The Bingham Plastic and Casson models are quantitatively similar. Both models contain two parameters, a yield stress \( (\tau_0) \) and a limiting viscosity \( (\mu_{\infty}) \), both exhibit shear thinning behaviour and both approach Newtonian behaviour as the shear rate or shear stress is increased. Concentrated slurries and suspensions normally exhibit an apparent yield stress resulting from the interparticle contact resistance in a rest state. Thus, although these models are quite simple mathematically, they exhibit proper limiting behaviour at both extremes of shear rate and are consequently very useful for representing the viscous properties of slurries and suspensions. The Bingham plastic model is the most commonly used in this regard.

The Herschel-Buckley model (sometimes referred to as the “yield Power Law” or general Bingham Plastic model) contains three parameters and is basically the Power Law model with an added yield stress parameter.
<table>
<thead>
<tr>
<th>Model</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Power Law</strong></td>
<td>$\tau = m\gamma^p$</td>
</tr>
<tr>
<td></td>
<td>$\eta(\gamma) = m\gamma^{p-1}$</td>
</tr>
<tr>
<td></td>
<td>$\eta(\tau) = m^{1/n}\tau^{(n-1)/n}$</td>
</tr>
<tr>
<td><strong>Bingham Plastic</strong></td>
<td>$\tau = \tau_o + \mu_\infty \gamma$</td>
</tr>
<tr>
<td></td>
<td>$\eta(\gamma) = \tau_o / \gamma + \mu_\infty$</td>
</tr>
<tr>
<td></td>
<td>$\eta(\tau) = \mu_\infty \tau / \tau - \tau_o$</td>
</tr>
<tr>
<td><strong>Casson</strong></td>
<td>$\tau^{1/2} = \tau_o^{1/2} + (\mu_c \tau)^{1/2}$</td>
</tr>
<tr>
<td></td>
<td>$\eta(\gamma) = [(\tau_c / \gamma)^{1/2} + \mu_c^{1/2}]^2$</td>
</tr>
<tr>
<td></td>
<td>$\eta(\tau) = \mu_c \tau / (\tau^{1/2} - \tau_c^{1/2})^2$</td>
</tr>
<tr>
<td><strong>Herschel - Bulkley</strong></td>
<td>$\tau = \tau_y + K\gamma^p$</td>
</tr>
<tr>
<td></td>
<td>$\eta(\gamma) = \tau_y / \gamma + K\gamma^{p-1}$</td>
</tr>
<tr>
<td></td>
<td>$\eta(\tau) = \tau(K / \tau - \tau_y)^{1/p}$</td>
</tr>
</tbody>
</table>

Table 1 Rheological models and their equations.
2.3.4. Definitions and measurements.

The rheological measurements were undertaken using a Discovery Hybrid Rheometer (DHR-2) from TA Instruments with cone and plate geometry in which the cone has an angle of 4°. Both, cone and plate had a diameter of 25 mm and while the cone was stainless steel the plates were aluminium disposable plates.

2.3.4.1. Viscosity and Shear-stress

Viscosity can be defined as the resistance of a body to be deformed, which in the case of fluids, is the resistance to flow[35]. Specifically, in this research, the dynamic (shear) viscosity was measured by applying an increasing shear-rate, from 1 to 500 s⁻¹ at 25°C, which expresses the resistance to shearing flows.

This measure is important for the mixing process as well as for the coating. A fluid with a high viscosity at low shear rates and lower viscosity at high shear rates will be easier to mix and it will better maintain the dispersion of the particles in it after the mixing is completed. The high viscosity at low shear rates improves the coating process in terms of obtaining better layers on the current collector and therefore reducing the cost by avoiding cut off waste[36].

The shear-rate, on the other hand, can be defined as the force per unit area that needs to be applied to maintain the shear rate[31]. As with the viscosity, the shear stress was measured by increasing the shear rate from 1 to 500 s⁻¹ at 25°C. In industrial processes high shear rates are applied, hence, it is of interest to know at what shear stresses the viscosity of the slurry will change [36].

2.3.4.2. Storage Modulus, Loss Modulus and Loss Factor (Tanδ)

For viscoelastic materials such as cured binders, the response to an applied stress is that some energy is stored elastically, as potential energy, and the remainder
is dissipated as heat. The energy dissipation causes the strain to be out of the phase with the applied stress by an angle, defined as the phase angle $\delta$ as it can be seen in Figure 2.4. The important feature of the rheometer is that the response of the sample is monitored, as a function of oscillatory load frequency, in terms of in-phase and out-of-phase components and using this data, the storage modulus (elastic behaviour), loss modulus (viscous behaviour) and the loss factor ($\tan \delta$) are determined.

The rheometer is based on the application of a small amplitude sinusoidal stress to the sample and the measurement of the resulting strain. The applied force and the resulting deformation both vary sinusoidally with time, the rates of which are specified by the frequency $f$ in cycles/second or $\omega = 2\pi f$ in radians/second.

For purely elastic materials, the strain will be exactly in phase with the applied stress due to the capacity of an elastic material to store mechanical energy with no dissipation of energy. For purely viscous materials, the strain will be 90 degrees out of phase with the applied stress due to the capacity of a viscous material to dissipate energy by flow but no storing capacity. It follows, therefore, that when a sinusoidal stress is applied to a viscoelastic material, the strain will be out of phase with the applied stress by an angle between zero and 90 degrees. This phase lag of the resulting strain ($\varepsilon_0$) behind the applied stress ($\sigma_0$) is illustrated in Figure 2.4 and is
quantified by the phase angle $\delta$. The magnitude of this phase angle is dependent on the amount of internal molecular motion occurring in the same frequency range as the imposed stress.

The stress ($\sigma$) and strain ($\varepsilon$) may be expressed as follows:

$$\sigma = \sigma_0 \sin (\omega t + \delta)$$

$$\varepsilon = \varepsilon_0 \sin(\omega t)$$

$\omega$ - angular frequency

$\delta$ - phase angle

Expanding Equation:

$$\sigma = \sigma_0 \sin(\omega t) \cos\delta + \sigma_0 \cos(\omega t) \sin\delta$$

The stress may be considered to consist of two components, one of which is in phase with the strain ($\sigma_0 \cos\delta$) and the other $90^\circ$ out of phase ($\sigma_0 \sin\delta$). By dividing both of these by the strain, the modulus can be separated into an in-phase (real) and out-of-phase (imaginary) component as follows:

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos\delta \quad \text{and} \quad E'' = \frac{\sigma_0}{\varepsilon_0} \sin\delta$$

$E'$ - real part of the modulus

$E''$ - imaginary part
The standard complex variable notation is:

\[ E^* = E' + iE' \]

where \( E^* \) is referred to as the tensile complex modulus.

This interpretation was based on the application of a sinusoidal tensile stress to the sample but is easily adopted to the application of a sinusoidal shear stress as follows:

\[ G^* = G' + iG'' \]

where \( G^* \) is the shear complex modulus, \( G' \) is the real part of the modulus and \( G'' \) is the imaginary part.

The phase angle \( \delta \) is given by:

\[ \tan \delta = \frac{G''}{G'} = \frac{\text{loss modulus}}{\text{storage modulus}} \]

The real parts of the moduli, \( E' \) and \( G' \), are called storage moduli as they quantify the material’s ability to store energy (elastic behaviour). The imaginary parts, \( E'' \) and \( G'' \), are called loss moduli and are a measure of the material’s ability to dissipate energy by flow (viscous behaviour). The loss tangent, \( \tan \delta \), is called the internal friction or damping (dimensionless parameter) and is the ratio of the energy dissipated to the energy stored per cycle.

The separation into two components of modulus, describing two independent processes within the material, is a feature that can be measured with the rheometer.
The Storage modulus \((G')\) measures the ability of the fluid to store energy (elastic behaviour) and the loss modulus \((G'')\) measures the ability of the fluid to dissipate the energy by flowing (viscous behaviour). They were measured in an amplitude sweep by increasing the oscillation strain from 1 to 20% while maintaining the angular frequency constant at 10 rad/s. Due to the hydrophobic nature of the carbon black and the limitations of the instrument it proved impossible to prevent the evaporation of water so it was decided to do it using that method because it was the fastest.

The loss factor \((\text{Tan}\delta)\) is the loss modulus divided by storage modulus, this is, \(\text{Tan}\delta = \frac{G''}{G'}\). Assuming that when \(G' > G''\), i.e. \(\text{Tan}\delta < 1\), means a solid like behaviour and the opposite, when \(G' < G''\) \((\text{Tan}\delta > 1)\), means a fluid like behaviour [9, 30] a \(\text{Tan}\delta\) higher than 1 is preferable. A more fluid like behaviour means a more dispersed slurry[28] but at the same time it means that it will flow faster and, therefore, lose any shape achieved during the coating process. So, a loss factor higher than one but close to it will ensure that while the slurry is dispersed it will not flow at low shear-rates[36], at least not too fast, and lose the shape before the drying process.

### 2.4. TGA

Thermogravimetric analysis (TGA) is a technique in which a sample’s weight is measured while it is being heated or cooled inside a furnace with a controlled temperature. In this way the mass change can be measured as a function of temperature, if the temperature increases or decreases, or time if the temperature remains constant[37].

The Differential Scanning Calorimetry (DSC) is a thermal analysis technique that looks at how a material’s heat capacity \((Cp)\) is changed by temperature. A sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow. An empty crucible is heated or cooled at the same time and at the same conditions as reference. This allows the detection of transitions such as melts, glass transitions, phase changes, and curing as well as chemical reactions that
are temperature dependent. Because of this flexibility, since most materials exhibit some sort of transitions, DSC is used in many industries, including pharmaceuticals, polymers, food, paper, printing, manufacturing, agriculture, semiconductors, and electronics[38].

If both techniques are combined, the mass loss or gain at every reaction that occurs when the temperature is changed or at a certain temperature over the time can be measured.

For this research the information obtained by the use of the Setaram TGA/DSC is important to know at what temperature will the anode materials start to degrade. This information is relevant for the drying process after casting the slurry on the collector as well as for the temperature changes that the battery can withstand during its usage cycle.

In this case the analysis was carried out by increasing the temperature 5°C per minute from 20 to 400°C and using N₂ as an inert gas and synthetic air. About 15 mg of the sample was weighted in an alumina crucible and an empty crucible was used as reference.
2.5. Casting onto current collector

In order to see the final composition of the slurries and their homogeneity once they are as they should be in the battery, the same procedure that will be used when manufacturing must be followed. There are plenty of choices when it comes to cast and dry [11, 20, 28, 39, 40], like the temperature, width of the cast, pressure, pressing etc. For this research the next procedure was chosen: the samples were casted onto an aluminium foil using a doctor blade with a width of 200 µm (the Na-CMC slurries, due to their low viscosity, had to be casted with a width of 400 µm). After that, they were dried in a conventional oven at 80°C for an hour and then dried overnight in a vacuum oven with a pressure of 300 mbar at 80°C to ensure complete evaporation of water.

2.6. SEM

The homogeneity of the casted slurry was observed using a Scanning Electron Microscope (SEM). The SEM is a powerful technique for examining a materials surface. In the microscope, electrons are directed through a series of lenses onto a sample. Many different types of electrons are then detected by various detectors. With the recent developments in the electron source and the advancement in the technologies of the detectors, higher resolutions have been achieved that can be utilised to examine beam sensitive material, nanomaterial and grain structure. The microscope used for this research is a Hitachi SU-70. Is a multipurpose, high resolution, scanning electron micro- scope with a thermal field emission source [41].
CHAPTER 3

RESULTS & DISCUSSION
3. Results and discussion

3.1. Degree of flocculation

The mixtures of the two binders, Na-alginate and Na-CMC, with DI-water, remained stable over 7 days with no phase separation or any settling observed for any of the binder concentrations (1%, 2% and 4% w/w).

When different carbon black mass loadings (1%, 2%, 3%, 4% and 5%) were added to the binder/water mixtures it was not possible to see any separation after 7 days, even though the carbon black is considered highly hydrophobic. Due to the lower density of the carbon black compared to water, it was expected that it would settle in the upper part of the suspension. Instead, after several weeks, when separation finally occurred, almost all of the carbon black settled at the lower part of the suspension (See Figure 3.1) with a small amount observed floating at the upper surface. This suggests that after the suspension was prepared agglomerates began to form between the carbon black particles and binder resulting in flocs which, had a higher density than water resulting in settling. The small amount observed on the upper surface is probably due to the hydrophobic nature of the carbon black. Alternatively it may have arisen from incomplete suspension during the initial mixing.

It should be noted that due to the colour of the carbon black the suspensions were so dark that it is possible that the “free” floating particles could have been present even before the phase separation was observed.
Figure 3.1 (1% w/w) Na-alginate and carbon black (5/5/0) suspension before and after separation.

When the graphite is added to the suspension, in the case of the Na-CMC, instead of the three components settling together, only the graphite could be found at the lower part of the suspension while the majority of the carbon black and the binder remained suspended (see Figure 3.2).

Figure 3.2 (1% w/w) Na-CMC Slurries (5/1/94) before and after settling

Figure 3.3 shows how the increase of the binder concentration in water reduces the degree of flocculation.
Figure 3.3 Degree of flocculation at different binder concentrations in water for different binder % as dry matter.

Figure 3.4 shows how the addition of carbon black increases the stability.

Figure 3.4 Degree of flocculation at different carbon black mass loadings. % referred to on a dry basis.
Figure 3.5 shows that increasing the binder percentage decreases the stability.

Figure 3.5 Degree of flocculation at different binder mass loadings. % referred to a dry basis

The addition of the graphite to the Na-alginate solutions makes them less stable. Due to the larger particle size of the graphite compared to carbon black, agglomerates are created allowing faster settling. After 2 days it was possible to see a small degree of separation between the clear part of the suspension and the agglomerated solids, after 7 days this separation became more evident (Figure 3.6) with some carbon black seen at the upper surface.

Figure 3.6 1.5% Na-alginate slurry (10/5/85) before and after separation.
The strongest effect was observed when the concentration (w/w %) of binder was changed. As shown in Figure 3.7, the degree of flocculation decreased when the concentration of Na-alginate in water was increased. As can be seen later, the viscosity also increases suggesting that the mobility of the particles, in this case the flocs, is inhibited by the intermolecular forces of the Na-alginate and need more time to finally settle.

![Figure 3.7](image)

**Figure 3.7** Degree of flocculation at different binder concentrations in water for different binder % as dry matter.

The ratio of each material (referred to on a dry basis) was observed to also affect the degree of flocculation. As can be seen in Figure 3.8 increasing the amount of carbon black, and therefore decreasing the mass of graphite, improves the stability of the suspension by lowering the degree of flocculation.
As previously stated, the graphite seems to break the balance of the intermolecular forces between the binder and the carbon black. Therefore, increasing the graphite component in the overall solids means that balance will be broken easier leading to a faster agglomeration of the particles and the consequent settling.

When the ratio of binder in the solid fraction is increased while maintaining the amount of carbon black constant, the degree of flocculation increases. In this case, as the percentage binder is increased the suspension stability decreases. As Figure 3.9 shows, when the binder ratio is increased, and even though the amount of graphite lowered, the degree of flocculation increased.
Figure 3.9 Degree of flocculation at different binder mass loadings. % referred to on a dry basis.

It seems, as commented earlier, that an important factor in determining the stability is the balance between the binder and carbon black. It can be seen that when more carbon black is present in the suspension the smaller the difference when the ratio of binder is changed.

3.2. Rheology

3.2.1. Viscosity and shear stress

At 1% w/w the Na-CMC behaves more likely as Newtonian fluid and it becomes more pseudoplastic, i.e. viscosity decreases as the shear rate is increased, this particularly noticeable at the higher concentration Figure 3.10.
Figure 3.10 Viscosity (a) and shear-stress (b) versus shear-rate plots of Na-CMC solutions at different concentrations

The viscosity and shear stress versus shear rates plots of Na-alginate solutions at 1 and 1.5% solid loading are presented in Figure 3.11. They both exhibit a shear-thinning behaviour. On the other hand, the shear stress increases with the shear rate, but the rate of it decreases more than in proportion to the shearing rate. This is called pseudoplastic behaviour. Figure 3.11 also shows how the viscosity and shear rate, both, increase when the concentration of the binder in water is increased.
Figure 3.11 Viscosity (a) and Shear-stress (b) versus shear-rate plots of Na-alginate solutions at different concentrations

For equal concentrations of binder the Na-CMC has a lower viscosity compared to Na-alginate as can be observed in Figure 3.12.
Figure 3.12 Viscosity (a) and Shear-stress (b) versus shear-rate plots of Na-CMC & Na-alginate solutions.

Figure 3.13 shows how the viscosity increases as more carbon black is added. It can be seen that the difference at low shear rates is more significant than at high shear rates. This behaviour suggests the formation of a network between the Na-alginate and carbon black that breaks, or at least weakens, as the shear rate is increased[42].
Figure 3.13 Viscosity (a) and Shear-stress (b) versus shear-rate plots of Na-alginate suspensions with different ratios of carbon black.

A further increase in viscosity can be observed in Figure 3.14 with the addition of the graphite. This increase is more apparent at low shear rates. This is probably due to the increased amount of solids and the settling of the slurry and the need to disperse it in order to make it flow.
Figure 3.14 Viscosity versus shear-rate plots of Na-CMC (a) and Na-alginate (b) suspensions (5/0/0, 5/1/0 and 5/1/94)

When the ratio of carbon black is changed, i.e. when more carbon black is added and the amount of graphite is decreased, it can be seen in Figure 3.15 how the viscosity at very low shear rates increases while the viscosity at high shear rates remains the same. A possible cause for this is the more extensive network created between the binder and the carbon black[42].
Figure 3.15 Viscosity versus shear-rate plots of Na-CMC (a) and Na-alginate (b) suspensions (5/1/94, 5/2.5/92.5 and 5/5/90)

Figure 3.16 shows that a suspension with only a 10% of the total mass, in which 5% is carbon black, has a higher viscosity at very low shear rates than one with the 100% of the total mass with a ratio of materials of 5/1/94. It suggests that the interaction between the binder and the carbon black has a more significant effect on the viscosity at very low shear rates than the effect of increasing mass loadings of graphite. This is probably due to the formation of a network between the two materials that is easier to break or weaken than making all the slurry flow as can be observed by the lower viscosity once the fluid has started to flow[42]. If the shear stress is observed, the force needed to make the suspension flow with the 100% of the mass loading is higher than the suspension with a 10% of the mass.
If the ratio of binder is increased, i.e. the amount of carbon black and graphite are lowered to increase the ratio of binder maintaining its concentration in water, it can be seen in Figure 3.17 that viscosity (at low shear rates) decreases. And this is due to the decrease of the total mass loading mentioned before.
As mentioned earlier all the rheological properties were measured 7 days after the slurries were prepared due to measurement of the degree of flocculation. In some cases, a small amount of sample was taken the same day they were prepared in order to investigate the effect of settling and remixing.

In the case of the Na-CMC it can be observed in Figure 3.18 (a) that the viscosities are almost the same just before making the slurry and seven days after. The fact that the carbon black and binder don’t settle, and the only material that needs to be dispersed is the graphite, may be the reason why shaking by hand for about 2 minutes is sufficient to achieve the same viscosity and stress.

Figure 3.17 Viscosity versus shear-rate plots of Na-CMC (a) and Na-alginate (b) suspensions (5/1/94, 8/1/91 and 10/1/89)
In Figure 3.18 (b) it can be observed that the viscosity is lower after settling and remixing specially at low shear rates. It should be mentioned that the slurries which had aged for 7 days had settled and required shaking for 2 minutes in order to re-suspend them. This suggests that they are unstable.

![Figure 3.18 Viscosity versus shear-rate plots of Na-CMC (a) and Na-alginate (b) suspensions (After mixing and 7 days later)](image)

**Figure 3.18** Viscosity versus shear-rate plots of Na-CMC (a) and Na-alginate (b) suspensions (After mixing and 7 days later)

**Figure 3.19** shows that there is a slight difference between the two mixing methods tested in this research. As can be seen the method 2 where all the components are added simultaneously and mixed for 48 hours exhibits a slightly
higher viscosity at low shear rates while the viscosity at high shear rates is almost the same.

Figure 3.19 Viscosity versus shear-rate plots of Na-CMC (a) and Na-alginate (b) suspensions (After mixing and 7 days later)

3.2.2. Loss Factor ($\tan \delta$), Loss Modulus and Storage Modulus

Figure 3.20 shows the loss factor for the 1% and 1.5% loading of (a) Na-CMC and (b) Na-alginate. Both the concentrations have $\tan \delta$ values greater than 1, indicating the loss modulus is higher than the storage modulus and therefore it behaves as a fluid[36]. It can also be observed that as the concentration increases the
Tanδ decreases meaning it has more outstanding characteristic of a network structure[42].

![Figure 3.20](image)

**Figure 3.20** Tanδ versus oscillation strain plot of Na-CMC (a) and Na-alginate (b) solutions at different concentrations.

**Figure 3.21** shows how the loss factor of the Na-CMC (a) and Na-alginate (b) decreases as more carbon black is added. In the case of the Na-CMC, the small difference between the three slurries suggests the effect of the increasing mass loading and probably the creation of a weak structure. For the Na-alginate that difference is larger suggesting that the network created between the Na-alginate and the carbon black becomes stronger[30].
Figure 3.21 Tanδ versus oscillation strain plot of Na-CMC (a) and Na-alginate (b) suspensions with different carbon black concentrations.

When the graphite is added to the Na-CMC suspension the loss factor decreases as shown in Figure 3.22 (a). In this case it decreases more when a 94% mass loading (graphite) is added than when a 1% the mass loading (carbon black) is added.

A different effect was observed in Figure 3.22 (b) when the graphite is added to the Na-alginate suspension where it can be seen that 1% of carbon black has a bigger effect than 94% of graphite. This suggests that the effect of the graphite may
simply be due to the mass loading rather than to any interaction between the particles.

Figure 3.22 Tanδ versus oscillation strain plot of Na-CMC (a) and Na-alginate (b) suspensions (5/0/0, 5/1/0 & 5/1/94)

Figure 3.23 shows how both loss and storage modulus increase when carbon black and graphite are added. As seen in the previous figure, the effect of the addition of the graphite is more significant. Due to big difference of mass between carbon black and graphite, this suggests that the change is due to the increase of the mass loading.
As Figure 3.24 shows, both loss and storage modulus increase but the loss modulus of the slurry increases more than the storage modulus emphasising its viscous behaviour.
Figure 3.24 Loss (a) and storage (b) modulus versus oscillation strain plots of Na-alginate suspensions (5/0/0, 5/1/0 and 5/1/94)

When the ratio of carbon black is increased, and the graphite lowered, the Tanδ decreases as it can be seen in Figure 3.25. This may be due to a more developed binder-carbon black network.
When the ratio of binder in the slurries is increased the loss factor increases as can be seen in Figure 3.26. Probably because when the ratio of binder is increased the total mass loading is reduced and therefore the strength of the binder-carbon black network is reduced.
Figure 3.26 Tanδ versus Oscillation Strain plot of Na-CMC (a) and Na-alginate (b) suspensions (5/1/94, 8/1/91 & 10/1/89)

Figure 3.27 shows how the loss factor is higher when the solution is mixed for the first time. This suggest that a proper mixing method must be carried out if the slurries are stored since a two minute hand shaking seems to be insufficient to restore give the original properties.
When the methods of preparing the slurries were compared it was observed that in the case of the Na-CMC, the difference is unappreciable as can be seen in Figure 3.28 (a). This difference probably would be larger with higher mass loadings.

In the case of the Na-alginate, as can be seen in Figure 3.28 (b) the difference is larger. This suggests a more extensive network structure between the Na-alginate and the carbon black. This is probably because in method 1, first, the binder and the carbon black are mixed creating the network between them and when the graphite is added, due to its larger particle size, it breaks this structure. On the other hand, in method 2, the three components of the slurry are mixed together and this network can be created, trapping some of the graphite inside in the process.
Figure 3.28 Tanδ versus oscillation strain plot of Na-CMC (a) and Na-alginate (b) slurries (5/1/94) mixed by different methods

3.3. TGA

In the case of the Na-CMC, as Figure 3.29 shows, the moisture evaporates when the sample is heated to 100°C and is about a 10% of the total mass.
The Na-CMC starts to degrade, with an exothermic reaction, at 260°C losing about a 40% of the mass. When the experiment is carried using synthetic air the exothermic peak at the temperature of the degradation is higher and sharper as shown in Figure 3.30.

Figure 3.29 TGA analysis of Na-CMC (used gas: Nitrogen)

Figure 3.30 TGA analysis of Na-CMC (used gas: synthetic air)
As it can be seen in Figure 3.31, when the temperature begins to increase, there is a slow loss of mass, about 15% up to 100ºC and 5% up to 200ºC, due to the moisture present in the sample. The endothermic nature of the liquid to gas transition can be observed in the heat flow from ambient temperature up to 100ºC when most of the moisture is evaporated.

![Graph of Na-Alginate](image)

**Figure 3.31** TGA analysis of Na-alginate (used gas: Nitrogen)

It seems to be stable up to 220ºC when an exothermic process occurs with a loss of 30% of the mass due to loss of volatile components, rupture of chain and fragmentation of Na-alginate[43]. Further heating to 400ºC resulted in an overall mass loss of 60%.

**Figure 3.32** shows how, when using synthetic air, the mass loss is the same as with nitrogen. The difference in this case is that the peak in the heat flow, at between 230ºC and 240ºC, is higher and sharper due to combustion, instead of the degradation that happens with nitrogen, which releases more energy.
In both cases, when air is used, the thermal decomposition may lead to the formation of \( \text{Na}_2\text{O} \) or \( \text{Na}_2\text{CO}_3 \)[26].

When a TGA is undertaken for a slurry, i.e. the complete anode with water, it can be seen in Figure 3.33 how an endothermic reaction occurs when it is heated to 100°C. This is due to the evaporation of all the water present in the slurry.

**Figure 3.32** TGA analysis of Na-alginate (used gas: synthetic air)

**Figure 3.33** TGA analysis of a Na-alginate slurry (used gas: nitrogen)
Is not possible to see any degradation of the binder because, overall, the amount of it is so little that the instrument is not sensitive enough to measure the change.

3.4. SEM

The main problem with Na-CMC, was that its low viscosity, at the concentrations used in this research, wasn’t sufficient to maintain the shape of the cast slurry and it tended to form droplets or bubbles. Figure 3.34 shows how after casting and drying they are present as empty spaces.

![Figure 3.34](image)

There were also black spots where it seems that the graphite had settled leaving only the carbon black and the binder on the surface. Because of this, in order to see the differences between the Na-CMC slurries, the SEM images were taken from parts that looked homogeneous.

As Figure 3.35 shows there is almost no difference between the two different concentrations. This is probably due to the very low viscosity of both concentrations such that it is not able to maintain the shape or the position of the particles in suspension, once the suspension is cast.
Figure 3.35 SEM Images of the 5/1/94 (Na-CMC) slurries. 1% wt. aq. (left) and 1.5% wt. aq. (right) (Magnification: x110)

The carbon black creates a network-like structure with the binder that can be found attached to the graphite particles and between them as shown in Figure 3.36.

Figure 3.36 SEM image of the 5/2.5/92.5 Na-CMC slurry (Magnification: x2.50k)

Increasing the ratio of carbon black fills the gaps between the graphite particles as Figure 3.37 shows.
As it can be seen in Figure 3.38 the Na-alginate slurries, after drying, seem to be homogeneous, without any agglomerates. The amorphous surface is due to the different shapes and sizes of the graphite particles which, under magnification (x110), are the only particles visible. It can be seen, as well, how increasing the concentration of the suspensions increases the porosity of the casted anode. This may be due to the faster settling, i.e. faster accommodation of the particles one over the other in the less concentrated solutions while the more concentrated suspensions have more capacity to maintain the particles in position during the drying process.
Figure 3.39 provides a closer view of the same slurries. It can be seen, as mentioned before, how the graphite particles are more tightly packed in the less concentrated slurries.

Figure 3.39 SEM Images of the 5/1/94 (Na-alginate) slurries. 1% wt. aq. (left) and 1.5% wt. aq. (right) (Magnification: x1.10k)

It can also be observed how the carbon black creates a network structure (a better view can be seen in Figure 3.40. Pieces of that structure can be found attached on the graphite particles and between them creating a link.

Figure 3.40 SEM Images of the 5/1/94 (left) and 6/2.5/91.5 (right) Na-alginate slurries (Magnification: x3.00k)
When the ratio of materials is changed, this is, when more carbon black is added and the amount of graphite reduced, it can be seen how the porosity decreases (see Figure 3.41), while the shape of surface remains almost the same.

![Figure 3.41 SEM images of the 5/1/94 (left) and 5/5/90 (right) Na-alginate slurries (Magnification: x110)](image1)

This is due to the carbon black filling the gaps between the graphite particles as it can be seen in Figure 3.42 which is a higher magnification of a slurry with 5% wt. (on a dry basis) of carbon black.

![Figure 3.42 SEM image of the 5/5/90 Na-alginate slurry (Magnification: x1.00k)](image2)
Figure 3.43 shows how the porosity increases if the amount of binder is increased.

Figure 3.43 SEM images of the 5/5/90 (left) and 6/5/89 (right) Na-alginate slurries (Magnification: x110)

This happens because in order to increase the ratio of the binder (on a dry basis) while maintaining its concentration in water, the amount of carbon black and graphite has to be decreased leading to lower solids occupying the same volume when the slurry is cast.

Figure 3.44 shows SEM images of the two slurries with the same ratio of material and concentration in water, but mixed using different methods. In this case, both look the same.

Figure 3.44 SEM images of the 5/2.5/92.5 Na-alginate slurries. Mixing method 1 (left) & method 2 (right)
CHAPTER 4

CONCLUSIONS
4. Conclusions

The aim of this research was to investigate the suitability of Na-alginate as binder for lithium ion battery anodes in terms of processing and manufacturing. Na-CMC, which has been investigated by other researchers, was used as a benchmark for comparison.

The degree of flocculation shows that for the same concentration of binder in water, Na-alginate has a better stability, e.g. for a solution of 5/1/94 Na-alginate has a degree of flocculation of 1.17 while for Na-CMC it was 1.90. Increasing the amount of carbon black lowers the degree of flocculation i.e. a suspension with a solid loading ratio of 5/5/90 was 1.04 and increasing the ratio of binder increases it, i.e. the 10/1/89 suspension had a degree of flocculation of 2.55.

The rheology measurements show that Na-alginate slurries have a higher viscosity e.g. at shear rate of 50 s\(^{-1}\) the suspensions of 1.5\% of binder in water and 5/1/94 of dry matter have a viscosity of 1.26 Pa\cdot s for Na-alginate and 0.20 Pa\cdot s for Na-CMC. The loss factor was lower for Na-Alginate, between 2 and 3 against between 2.9 and 3.3 for Na-CMC, showing a more developed structure.

From the TGA results can be seen that Na-CMC is more temperature stable because it starts to degrade at 260\(^{\circ}\)C while the Na-alginate starts at 220\(^{\circ}\)C. The SEM images and mostly the casting and drying process, demonstrated that while 1.5\% Na-CMC in water wasn’t enough viscous to cast the slurries it was possible to do it with Na-alginate showing a homogenous electrode and maintaining the shape given.

Partners in the project in UL tested the electrochemical behaviour of Na-CMC and Na-alginate finding that Na-CMC has a performance similar to PVdF while Na-alginate exhibits an improved performance for half- cells consisting only in binder and active material[44]

Therefore this research concludes the suitability of the Na-alginate as binder for lithium ion battery anodes in terms of processing and manufacturing the electrodes.

It is recommended to find the proper concentration of binder as well as a proper ratio of dry material.
5. References


