The effect of nanocellulose on PVDF/Carbon Black in the fabrication of conductive thin films for electrochemical applications

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LIST OF ABBREVIATION

CB	Carbon black
CV	Cyclic voltammetry
PVDF	Polyvinylidene difluoride
CNF	Cellulose nanofiber
KOH	Potassium hydroxide
MW	Molecular weight
LiCl	Lithium chloride

ABSTRAK

Filem nipis berasaskan selulosa yang fleksibel dan berdiri bebas telah disediakan melalui dua kaedah untuk digunakan dalam pelbagai aplikasi elektrokimia. Kaedah pertama yang melibatkan pengadunan nanoselulosa dengan PVDF dan karbon hitam telah menunjukkan respon elektrokimia yang memuaskan pada kadar imbasan yang sangat rendah iaitu 0.005 V/s atau 0.5 mV/s. Kandungan CNF yang rendah sebanyak 10 wt% adalah memadai untuk menjana ciri fleksibel sambil mengekalkan konduktiviti filem, manakala kandungan CNF yang lebih tinggi meningkatkan rintangan filem. Salutan filem CNF dalam dakwat konduktif PVDF/CB menunjukkan ujian CV yang berjaya ke atas pelbagai kadar imbasan. Kehadiran LiCl semasa penyediaan filem CNF telah meningkatkan prestasi elektrokimia filem yang diukur dengan ketara. Walaupun pemuatan karbon mampu meningkatkan kekonduksian, kemampuan lekatan dakwat konduktif pada substrat sangat bergantung pada pengikat PVDF. Filem nanoselulosa dengan 20% berat LiCl dan nisbah 5 hingga 5 dakwat konduktif PVDF/CB terbukti mempunyai prestasi elektrokimia yang baik berdasarkan tindak balas semasa dan luas CV yang diperolehi. Tindak balas arus tertinggi telah direkodkan pada potensi penggunaan maksimum 0.6 V, manakala yang paling rendah ialah -0.3 V. Lenturan menunjukkan peningkatan dalam rintangan, sekali gus menunjukkan pengurangan kekonduksian, namun masih boleh digunakan semula selepas diuji dengan CV.

ABSTRACT

Flexible and freestanding cellulose-based thin films have been prepared via two methods for use in various electrochemical applications. The first method involving the blending of nanocellulose with PVDF and the added carbon black has shown satisfactory electrochemical behaviour at a very low scan rate of 0.005 V/s or 0.5 mV/s. Low content of CNF of 10 wt% is adequate for generating flexible features while retaining the conductivity of the film, whereas higher CNF content increases film resistance. The coating of CNF film in PVDF/CB conductive ink shows a successful CV test over a wide range of scan rates. The presence of LiCl during the preparation of CNF film has significantly increased the electrochemical behaviour of the measured film. Even though carbon loading should increase conductivity, adhesion on the coated substrate is most dependent on the PVDF binder. The nanocellulose film with 20 wt% of LiCl and a 5 to 5 ratio of PVDF/CB conductive inks proves to have good electrochemical performance based on the current response and the area of the CV obtained. The highest current response was recorded at the maximum applied potential of 0.6 V, whereas the lowest was at -0.3 V. The bending reveals the increment in resistivity, thus indicating a reduction in conductivity, though it is able to be used again after being tested with CV.

CHAPTER 1 INTRODUCTION

The first chapter describes the synthesize of conductive ink for the fabrication of conductive thin film and emphasises the influence of nanocellulose to enhance its properties. In general, this chapter summarises the significant features of nanocellulose-based conductive thin film to be used for electrochemical applications. This chapter also contains the problem statement and research objectives for this study.

1.1 Background

Recently, conductive ink has gained much attention due to the vast improvement in the manufacturing of electronics devices where the transition occurs due to the need of developing a device that are thin in size, flexible and wearable (Tran, Dutta and Choudhury, 2018). Many researchers have conducted numerous studies regarding conductive ink which proven by the graph below that shows the linear trend in the number of publications involving conductive ink from 2010 until 2020. The data was obtained from the Scopus database for conductive ink search terms. The use of conductive ink as a self-standing conductive film has been studied for many years since the fabrication process is simple and inexpensive.

There are three main components that formulate a conductive ink including the conductive material, a binder agent that allow the conductive particles to be aggregated efficiently and a solvent that suspends other components and imparts the desired viscosity to the ink. (Camargo *et al.*, 2021). A conductive component that commonly being used include metal and carbon-based conductive ink. Nonetheless, carbon-based conductive ink such as graphite (Kim *et al.*, 2021), graphene (Chu *et al.*, 2021), carbon nanotube (Oliveira and Pereira, 2021) are more well-established due to chemical inertness, high electrical and thermic conductivity. Though, the major difference between these materials that need to be considered before being adopted in industry is the cost.

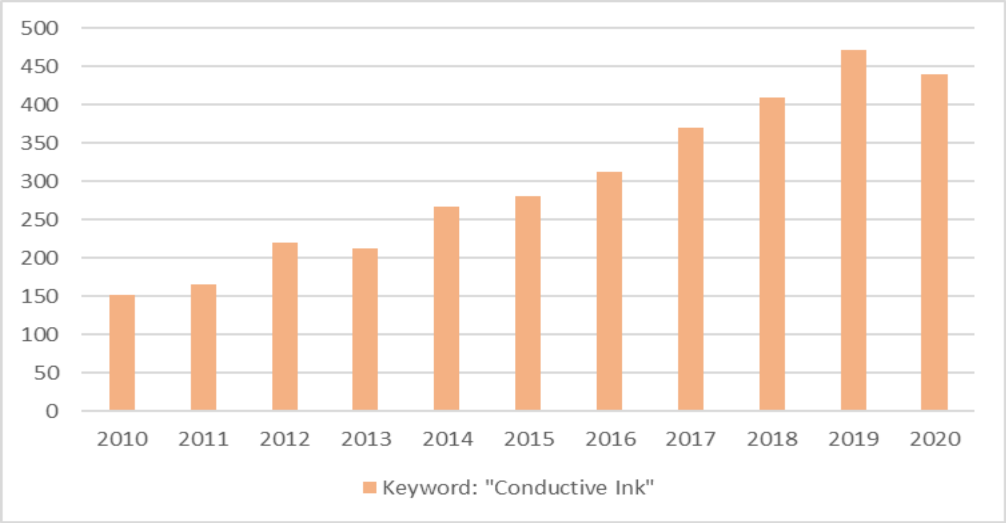

Figure 1: A year by year increase in the number of publications on conductive ink in 2010-2020 (under the keywords “conductive ink” in Scopus database limited within article title, abstract and keywords)

Nanocellulose is a material with a size of 100 nm or less, a very high specific area, high porosity with excellent pore interconnectivity, low weight, and great biodegradability (Hernandez et al., 2018). Nanocellulose can derived from a renewable resource and possesses unique properties of tunable surface chemistry (Kumar and Kumar, 2022). Recently, due to excellent features of high transparency, stiffness, flexibility, low thermal expansion, tunable rheology as well as ability to extend self-assembly into multiphase polymer networks, nanocellulose with at least one nanoscale lateral dimension have been utilized for electrochemical devices (Tayeb and H. Tayeb, 2019). In addition to its outstanding properties, the abundancy of nanocellulose made them easier to be extracted in various type of plant that present as a biological nanocomposite structure of the plant cell wall. The elementary fibrils are the basic organizational units of plant cellulose that are just 3−4 nm wide, which are combined to form 10−30 nm wide microfibrils (Wang and Drzal, 2012). Additionally, cellulose can be disintegrated into microfibrils through mechanical process which have different names such as microfibrillated cellulose, cellulose nanofiber, nanofibril, nano fibrillated cellulose and nanocellulose. All are referring to the same nanocellulose though the main difference lies on the degree of fibrillation. In this work, the terms stick to cellulose nanofiber (CNF) to represent the fibrillated nanocellulose and does not involve the crystalline form of nanocellulose or known as cellulose nanocrystals (CNC). The flexibility and plasticity are attributed by the amorphous region of nanocellulose whereas the crystalline region responsible for the stiffness and elasticity (Onyango, 2021).

Conductive nanomaterials have attracted considerable interest in this regard, as they offer excellent electronic properties and high compatibility (González-Domínguez *et al.*, 2021). When it comes to the most well studied nanostructures in terms of their electrical, thermal and mechanical properties, carbon nanotubes (CNTs) and graphene derivatives stand out among others carbon materials. Out of the variety of carbon-based conductive materials, carbon black is most widely used carbon fillers that exhibit higher electrical conductivity, high surface area, and stability (Gautam and Verma, 2018). Carbon black has been utilised as a reinforcing component in vehicle tyres and rubber automotive products, while inks, paints, plastics, and coatings are typical everyday products that contain carbon black. Carbon black is produced by partial combustion or thermal breakdown of gaseous or liquid hydrocarbons under prescribed conditions, yielding a range of carbon black grades with varying characteristics (e.g., specific surface area, particle size and structure, conductivity, and color) (Tofighy and Mohammadi, 2019). With the combination of conductive materials with nanocellulose, it has a significant impact on the mechanical structure of the composite which also lead to flexibility features while retaining the conductivity behaviour as reported in many literature.

Polymer blending is a versatile approach that utilises the properties of individual polymers to obtain cost savings, mechanical property enhancements, and increased flexibility of polymer blend films (Sachin, Haridass and Ramanujam, 2020). The blend of these two polymeric materials can result in more enhanced properties while retaining the special properties of each polymer. Additionally, the blend of PVDF with other polymer has been studied extensively to produce an advanced material that consist of the combined properties of toughness and piezoelectric nature of PVDF along with the rigidity and optical properties of the composite (Wu *et al.*, 2020). Thus, this project tends to focus on the compatibility of nanocellulose to be used as reinforcing agent in blending with PVDF polymer. Moreover, as a biodegradable materials, cellulose can be constructed as a substrate to be used in flexible and green electronics (Jia *et al.*, 2022). Hence, the PVDF and conductive materials can be made as conductive ink to coat on nanocellulose thin film.

1.2 Problem Statement

The binding of polymers and conductive materials is widely discussed in the literature. In terms of conductivity, the fabricated film based on the combination of those two materials should be able to achieve the conductivity behaviour. Additionally, there are also studies on the nanoparticles to further enhance the conductivity of the film. In order to make the fabricated film applicable in various electrochemical applications, one of the interesting features that have been desired properties of the conductive film is the enhanced mechanical structure, specifically on the flexibility of the film. Over the past few years, the research on nanocellulose has been done tremendously as it proves to exhibit a good mechanical structure owing to the abundancy of the hydroxyl groups. In this light, the presence of nanocellulose can aid in achieving enhanced mechanical properties of the film. However, homogeneous dispersion within a polymeric matrix is difficult to achieve as cellulose nanoparticles have a strong tendency for self-association due to the omnipresence of interacting surface hydroxyl groups (Dufresne, 2013). The compatibility of the nanocellulose with other polymer causing a doubt whether it could be well mixed with the PVDF polymer and having a good molecular interaction.

Apart from blending method, nanocellulose may also be used as a substrate that allows a conductive layer to be coated on top of the film. The cyclic voltammetry analysis will determine the workability of the films that will be fabricated through blending and coating approach to be used for electrochemical application.

1.3 Objective

1. To prepare a PVDF/CB conductive film incorporated with nanocellulose through blending and coating method.
2. To observe the effect of nanocellulose in the PVDF/CB conductive ink on the mechanical structure of the fabricated film.
3. To study and compare voltammetry response of the conductive films with variation of parameter such as concentration of nanocellulose, presence of LiCl and carbon black loading.

1.4 Sustainability

This present work focuses on the presence of CNF in the fabrication of flexible conductive thin film. However, the conductive filler used is carbon black, which known to be a toxic material. The control of the ratio between polymer matrix and conductive filler could reduce the consumption of carbon without affecting the decreased in conductivity.

Following the 9th sustainability goal focusing on industry, innovation, and infrastructure, this research project sheds light on how technologies can be used. As electrochemical application has gained attention due to advancement of technologies especially in the development of wearable devices, the findings in this area can help in improving the current state of technology to another level, which is worth the amount of money invested in the research.

Another element of sustainability goals that can be related to this project is the 7th goal; affordable and clean energy. Due to the abundancy of nanocellulose, the thin film produced is definitely cheap in price and suitable to be used in various electrochemical applications. However, as the amount of cellulose does not contribute to conductivity, the cost might be affected the most by conductive filler. The nanoparticles that have gained serious attention recently is considered to be high in demand and thus, the cost is significantly higher and incomparable with those binder polymers. As research advances, high conductivity films with less conductive fillers are becoming an interesting area for development and thus, optimizing the overall cost of fabrication.

Following the 12th sustainability goal, which is responsible consumption and production, the use of bio-based materials in the production of electronic devices will definitely serve as a mitigation measure in the reduction of toxic waste and pollutants. According to the goals, it is targeted to support developing countries to move towards more sustainable patterns of consumption by 2030 by encouraging industries, businesses and consumers to recycle and reduce waste. This also coincided with the fabricated conductive thin film of this project, as a good CV response curve was presentable after 500 times of bending, even though the results suggest that electrochemical performance reduces upon bending. Still, it is a good start to continue further research on how to maintain the conductivity in electrochemical analysis to ensure its longevity.

CHAPTER 2 LITERATURE REVIEW

Chapter 2 presents the literature review of this study. The detailed properties of PVDF and nanocellulose is discussed to understand their unique properties in order to blend both polymers to be used in the preparation of conductive ink. The enhanced properties due to the addition of nanocellulose in the structure and the effect on its conductivity properties will be reviewed in this chapter as well.

2.1 Effect of PVDF in the preparation of conductive ink

PVDF is a semicrystalline flouropolymer that is both semicrystalline and thermoplastic. Because of its high mechanical, thermal, and chemical resilience, this polymer has sparked a lot of interest in electrochemical applications. PVDF comes in a variety of crystalline polymorphs, including Alpha (α), Beta (β), Gamma (γ), Delta (δ), and Epsilon (ε) (Rajeevan, John and George, 2021). PVDF was used in the majority of the studies because of its unusual piezoelectric characteristics. As a result, this polymer is known to have both mechanical and electrical properties. The molecular structure of PVDF in its common crystalline structural form in the α, β and γ phases is depicted in the **Figure 2** below. The crystalline polymorph's alpha phase does not have good piezoelectric capabilities, but it is thermodynamically stable (Lozano and Mohan, 2021). The polar crystal structures of beta, gamma, and delta phases enable them to show piezolelectric characteristics. The β-phase of PVDF is the most distinct of the three, including piezoelectric, pyroelectric, and ferroelectric features as well as the strongest piezoelectric response (Rajeevan, John and George, 2021). When an external load is applied, the material's ability to convert internal elastic energy to dielectric energy is referred to as piezoelectricity (Kalimuldina *et al.*, 2020). The β-phase of PVDF may be seen in the picture below to have a planar zigzag layout, which is known to be important for exhibiting the highest piezoelectricity. Due to the electronegativity of fluorine atoms as contrasted to hydrogen and carbon atoms, the piezoelectric characteristics of PVDF are strongly connected to the significant electric dipole moment of the PVDF monomer unit (CH_2-CH_2) (Wu *et al.*, 2020).

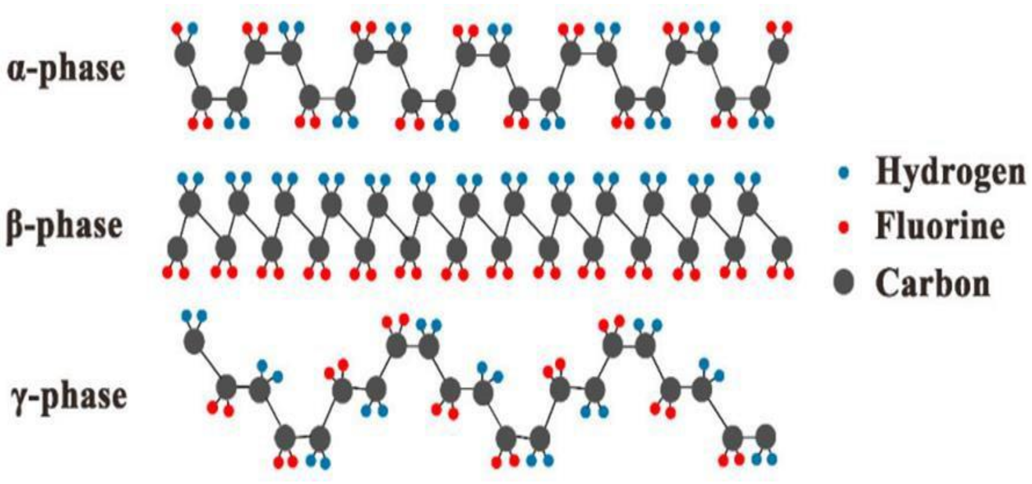

Figure 2 Molecular structure of alpha, beta and gamma phase of PVDF (Wu et al., 2020)

In the reported work by (Oneide *et al.*, 2021), the addition of gold nanoparticles (AuNPs) to PVDF has caused the α-crystalline structure to disappear. It was discovered that there is an interaction between gold nanoparticles and the PVDF α-phase, which results in the crystallisation being reduced to the β-phase only. The effect of conductive polymer on the thermal conductivity of the PVDF/Polyaniline (PANI)-nanofibre composite membrane is shown in another study by (Guo *et al.*, 2018). The features of the b-phase after the addition of 50 wt% and 60 wt% PANI may be observed from XRD patterns. It was claimed that the presence of PANI nanofibers in the α-phase form of PVDF damaged the metastable structure, causing the PVDF molecule to rearrange into a more stable β-phase form. The thermal conductivity of the membrane was observed to rise dramatically when a significant concentration of PANI (up to 50 wt%) was added due to the interaction between PANI-nanofiber and the PVDF matrix. When the PANI content exceeds 50 wt%, the thermal conductivity begins to decline. As a result, it can be determined that the inclusion of nanofillers and conductive polymer can influence the crystallisation form of PVDF, with their interaction causing a change in PVDF's β-phase form.

To combine the attractive electrical properties of conductive nanofillers with the good mechanical responsiveness of polymeric materials, conductive fillers are always incorporated into the polymer matrix. Various nanofillers, such as graphene (Gr), carbon nanotubes (CNTs) and nanofibers have been synthesised and researched to produce polymer films to optimize piezo response in polymer materials (Kalimuldina *et al.*, 2020). Consequently, the strong mechanical properties of PVDF make it appropriate for nanocomposite manufacturing. According to Patel and Kumar (2020), adding nanofillers to the polymer electrolyte reduces the degree of crystallinity, resulting in an amorphous phase when the filler concentration is increased. The effect of TiO_2 nanoparticle dispersion on the electrical conductivity of solid polymer electrolytes was investigated in their studies. The results show that the melting temperature drops due to the presence of TiO_2 nanoparticles.

2.2 Properties of nanocellulose

Since cellulose is abundant and has desirable qualities like as high specific surface area, natural fibre shape, biocompatibility, and several fabrication processes, nanocellulose is rapidly becoming a smart alternative for a wide variety of applications

(Ilyas *et al.*, 2020). Cellulose can be extracted from numerous sources including plants, trees, tunicates, and bacteria. The properties of nanocellulose mainly depend on fabrication route, processing conditions, and the source of cellulose (Illa, Adepu and Khandelwal, 2022). Nanocellulose can be classified into two main types, cellulose nanocrystal (CNC) and cellulose nanofiber (CNF) which differ in terms of amorphous portion and dimension. The cellulose chain consists of two region, crystalline and amorphous. CNC have nanodimensions in both length and diameter, whereas CNF have length in microdimensions and diameter in nanodimensions (Gopakumar, Thomas and Grohens, 2016). Crystalline region exhibits high order of microfibrils while less order of microfibrils is known as amorphous. That being said, the structure of CNC is solid due to lack of amorphous whereas CNF is typically a cellulose in nano size. Cellulose nanocrystal can be extracted from cellulose fibrils by chemical treatment such as acid hydrolysis to hydrolyze and remove the amorphous region while maintaining the crystalline parts (Phanthong *et al.*, 2018). The extraction process of CNC and CNF were depicted in **Figure 2** and **Figure 3** respectively as schematic diagram. Consequently, cellulose nanofiber is resulted from mechanical treatment of the cellulose chain. CNF still have both crystalline and amorphous region that also contain 100% of cellulose chemical composition (Dufresne, 2013). Compared to nanocrystalline cellulose, nanofibrillated cellulose has a longer length, a high aspect ratio (length to diameter), a large surface area, and a high concentration of hydroxyl groups that makes it readily accessible for surface modification. (Phanthong *et al.*, 2018).

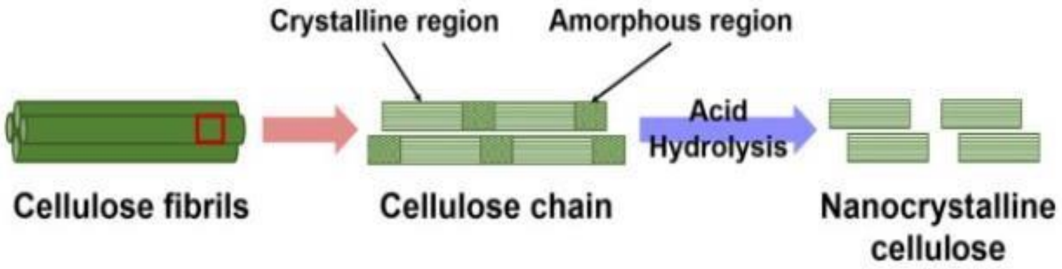

Figure 3 Schematic of the extraction of nanocrystalline cellulose (Phanthong et al., 2018)

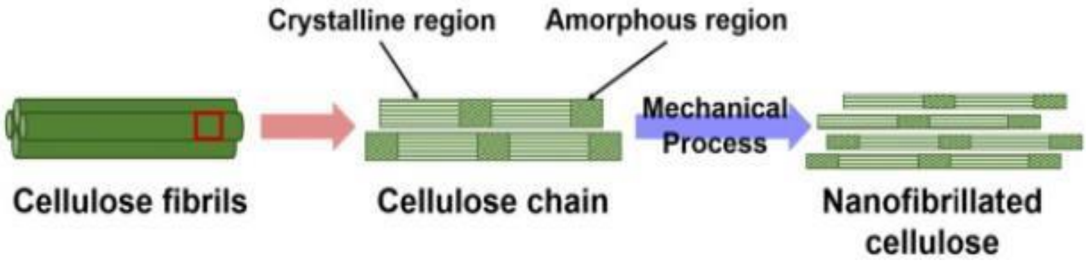

Figure 4 Schematic of the extraction of nanofibrillated (Phanthong et al., 2018).

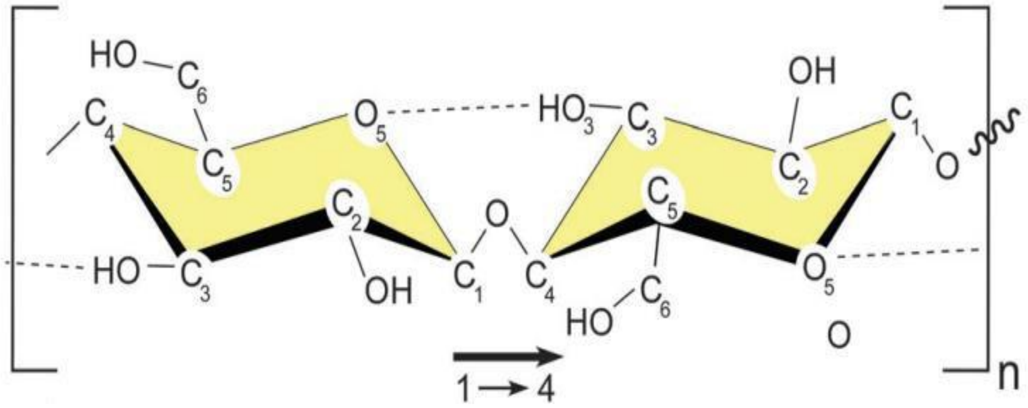

Figure 5 Schematic of cellulose repeating unit with the β-(1,4)-glycosidic linkage, dotted lines indicate intramolecular hydrogen bonds

Figure 5 shows the molecular view of the cellulose repeating unit with the β-(1,4)-glycosidic linkage. Intrachain hydrogen bonding between hydroxyl groups and oxygens of adjacent ring molecules stabilizes the linkage and resulting in the linear structure of the cellulose chain (Moon *et al.*, 2011). It was further explained that the van der Waals and intermolecular hydrogen bonding between adjacent molecules promotes parallel stacking of multiple cellulose chains forming elementary fibrils that further aggregate into larger microfibrils (5-50 nm in diameter and several microns in length). The stiffness of this stable polymer is attributed by those intra and inter-chain hydrogen bonding. It is worth mentioning that hydrogen bond among the OH groups in CNF that electrostatically attract to each other cause the cellulose chains to build an ordered structure.

The application of nanocellulose in nanocomposite is possible with the knowledge of the possible interaction between nanocellulose and the substrate. This is the case for coating method where the adhesion mechanism is crucial in order to produce a nanocomposite with enhanced mechanical structure. Hydrogen bonds and van der Waals forces are regarded as the most prominent intermolecular forces contributing to adhesion strength, though it is not entirely understood which one is of primary importance that contributes the most to the strength of binding (Tayeb *et al.*, 2018). The existence of hydrogen bonds between hydroxyl groups on adjacent cellulose surfaces plays a significant role in the exceptional adhesion qualities between cellulose fibres and makes CNF an attractive binder material for nanocomposites (Tayeb *et al.*, 2018). In a case of the adhesion between cellulose fibers are influenced by the contributions of friction, interfibrillar water structure, hydrogen bonds, van der Waal forces as well as electrostatic linkages (Fornué et al., 2011). However, many researchers having a doubt on those factors as to be the main contribution of adhesion between cellulosic surfaces in contact. Additional theories that are believed to be the superior factor have been proposed by Gardner *et al.,* (2008). The theories include the mechanical interlocking, intermolecular diffusion and chemical interactions.

Mechanical interlocking was due to the irregular surfaces, molecular chains interaction between cellulosic surfaces lead to intermolecular diffusion and chemical interactions attributed to acid-base interactions, hydrogen bonding, van der Waals and electrostatic forces.

2.3 Method of nanocellulose extraction

The extraction of nanocellulose can be conducted via various method. As for the nanofibrillated cellulose or cellulose nanofiber, the focus shall be on mechanical treatment even though combined method is also possible. The method of cryocrushing involves the mechanical method used to break the cellulose wall into nanosize fibers. This method has been demonstrated by Chakraborty, Sain and Kortschot (2005), starting from refining process, followed with cryocrushing under liquid nitrogen and proceed with either freeze-dried or suspended in water before going through morphology characterization (Chakraborty, Sain and Kortschot, 2005). Based on the optical microscopy, it was believed that the microfibrils have the potential in the production of high-strength nanocomposites according to the aspect ratio measurement. The ability to disperse in the polymer matrix was confirmed through laser confocal microscopy. Another common mechanical method is high pressure homogenization by which the cellulose fiber-water suspension was passing through a very narrow channel under high pressure (Wang *et al.*, 2017). Some advantages include high efficiency, simplicity, and cheaper cost as compared to other options.

2.4 Variation of method to combine nanocellulose with conductive filler

There are many methods to combine the nanocellulose with conductive materials from the complex that involves the functionalization of nanocellulose surface to the easiest such as direct blending followed by stirring and drying. The extraction sources and techniques have a significant impact on the physicochemical properties of nanocellulose (Patil *et al.*, 2022). Therefore, the selection of method of extraction is important depending the specific properties of desired nanocellulose.

For the coating method, nanocellulose was prepared prior to the adhesion of the coating materials, usually in a slurry solution or viscous ink. There is also a report work regarding the coating of electroless nickel on nanocellulose that has been activated by different activation solutions consisting of $NiSO_4$, HCl, $NaBH_4$ and NaOH under the conditions of pH 9 at 60°C for 15 min (Pan *et al.*, 2016). Nanocellulose in fibrillated form can also be utilized as a substrate for various applications. Screen printing of conductive filler was possible to produce a cellulose-based conductive film. For instance, Pammo *et al.*, (2019) have developed mechanical fibrillation methods for the preparation of microfibrillated cellulose (MFC) films using hot-plate evaporation techniques (Pammo *et al.*, 2019). MFC was first diluted with deionized water to obtain more evenly distributed MFC films. The hot plate was set to 50°C and the drying time was fixed to one day at room temperature. The homogenous MFC solution was then poured on a polyethylene terephthalate (PET), and consequently, the MFC film was torn off from the PET substrate after drying. Using a screen-printing technique, the conducting graphite ink was fabricated on MCF and also PET film, which served as references. The films were dried in a convection oven at 100°C for 1 hour after screen printing. Results obtained suggested that the thickness of the film is highly related to the absorption of the ink into the film. With sheet resistance measurement, the film with the greatest thickness showed the lowest sheet resistance measurement, which also indicates higher conductivity compared to PET film. This was deduced by the authors that MFC film is more porous than PET film, thus affecting the absorbed portion of ink into the film.

Besides, the conductive material can be incorporated in nanocellulose via in situ polymerization. In situ polymerization methods generally involve the mixing of nanomaterial in a neat monomer (or multiple monomers) or a solution of monomer, followed by polymerization in the presence of the dispersed nanomaterials (Potts *et al.*, 2012). This technique is a particularly important method for the preparation of composites with insoluble or thermal unstable polymers as a matrix because such matrices cannot be dissolved in solvents or fused (Tang *et al.*, 2019). Wang *et al*., (2015) have successfully demonstrated an approach in the preparation of paper electrodes consist of polypyrrole, nanocellulose and graphene oxide with on 5.8 wt% of conductive filler via a facile in situ chemical polymerization method (Wang *et al*., 2015). On top of that, the produced film was self-standing, binder-free, dense and flexible in terms of mechanical structure with also reported to have the largest volumetric capacitance of 198 F cm^{-3} among flexible electroactive conducting polymer, ECP-based electrodes. A blending of amphiphilic CNFs with graphite have been reported by Paquin *et al.*, (2015) where the nanocellulose was utilized as a exfoliating agent and a surfactant to produce high quality graphene from graphite (Paquin *et al.*, 2015). The fabricated graphene/CNF film was successfully exhibited a good electrical conductivity by which influenced by the blending speed that affecting graphene sizes and layers.

Controlling the thickness of the layer through blending or coating poses the greatest difficulty in the variation of the approach (Hsu and Zhong, 2019). As not all conductive materials are compatible with having a molecular interaction with nanocellulose, a well-dispersed morphology also restricts the production of films with high conductivity. The same authors further added that coating/blending, inkjet printing, and in situ polymerization are the most popular approaches for fabricating cellulose-based conductive membranes because they entail convenient techniques which does not require the use of advanced equipment or special conditions.

2.5 Properties of the nanocellulose combined with conductive filler

The addition of nanocellulose can improve the mechanical properties of the composite film, as mentioned previously. Due to the advantages of nanocellulose, its combination with a polymer matrix may result in a nanocomposite with exceptional mechanical properties. The creation of this network is dependent on the homogenous dispersion of the filler, the percolation threshold that depends on the aspect ratio of the nanoparticles, and the filler/filler interactions' strength (Dufresne, 2013).

In the fabrication of composite conductive films, the mechanical properties can also be shown through the measurement of tensile strength. A composite of cellulose and nanocellulose reinforced polyvinyl alcohol (PVA) has been prepared by Sultana *et al.*, (2020) The tensile properties of the composite were then determined by measuring with a universal tensile testing machine. Based on the measurement, nanocellulose reinforced PVA composite showed higher tensile strength than cellulose-PVA composite, which was consistent for every fiber loading of 1, 2, 3, 4 and 5 wt%. This also proves the good dispersion of nanofiber in PVA matrix and good interfacial adhesion between PVA and nanocellulose. Ding, Tang and Zhu (2022) reported work on the fabrication of the composite films using cellulose nanocrystal reduced graphene oxide as the conductive filler (Ding, Tang and Zhu, 2022). From their work, it is revealed that the composite films have successfully been fabricated with a high specific capacitance and tensile strength. The RGO film with 50% CNC content had a tensile strength of 59.08 Mpa, which was four times higher than the RGO film without CNC. The amount or concentration of the conductive filler may affect the mechanical strength of the composite film. This is connected to the interaction between the conductive filler and the polymer matrix. The study conducted by Du *et al.*, (2022) shows the result of the strain-stress curves of PEDOT: PSS/CNP samples with different PEDOT: PSS loadings that suggest the increasing PEDOT: PSS ratio causes the produced film to have reducing mechanical strength properties (Du *et al.*, 2022). PEDOT: PSS is the commonly used conductive polymer where it has been successfully blended with CNF through polymerization. The main reason lies in the fact that the mechanical strength of the film is mainly contributed to by the existence of hydrogen bonding among the CNFs. Research conducted by Dias *et al.*, (2019) shows the grafting of polythiophene on nanofibrillated cellulose (NFC) film while retaining good electrical conduction (Dias *et al.*, 2019). Polythiophene is an advanced biomaterial that is known to be highly conductive and possesses good chemical and thermal stability. (Haoran Liu *et al.*, 2019). The NFC film was prepared through dilution with water beforehand, followed by vacuum filtration and drying for 48 hours. The grafting is done on NFC film via polymerization of thiophene monomer. The results of the experiment suggest an increase in electrical conductivity from 9.40×10^{-3} to 133 μS cm^{-1}. However, the mechanical properties were said to be slightly reduced due to the polythiophene grafting, which caused the interaction of the thiophene sulphur group with the hydroxyl groups of NFC, resulting in a decrease in the elongation of the films after mechanical testing.

From a structural point of view, the high cellulose content of both raw materials gave the CNF films great physical and chemical properties. Due to a dense network of intramolecular and intermolecular hydrogen bonds between the chain, cellulose fibrils have a highly crystalline structure and are firmly packed together (Hassan *et al.*, 2021). Some reported work employing carbon-based materials such as carbon nanotubes and graphene incorporated with nanocellulose in the fabrication of composite film reveals the influence of dispersion on the structure and conductivity. For instance, Koga *et al.*, (2013) have found that the blend of carbon nanotubes (CNT) and cellulose nanofibrils (CNF) results in some physical entanglements due to the similarity in microstructure of both CNT and CNF. As a result, CNT can easily absorb onto the skeleton of the CNF network and form a complete filler network. It could imply that any conductive filler and polymer with a comparable microstructure can be blended successfully.

In addition, Viannie *et al.*, (2021) noted that the homogeneous dispersion of the conductive filler is crucial to the electrical and mechanical properties of nanocomposites (Viannie *et al.*, 2021). During the fabrication of PDMS/MWCNT nanocomposite sheets, the best homogeneous dispersion was achieved at filler concentrations of less than 6%. It was supported by morphological examination of the composite using a Field Emission Scanning Electron Microscope (FE-SEM). As a result, the filler concentration has a considerable effect on the electrical conductivity of the PDMS/MWCNT nanocomposite due to the good dispersion. Due to the high aspect ratios and surface area of MWCNTs, the percolation threshold was reached at concentrations significantly lower than those of other conductive nanoparticles, resulting in the nanocomposite's enhanced mechanical strength without sacrificing its electrical conductivity.

Furthermore, in order to achieve a homogeneous dispersion, the mixture must also be thoroughly mixed with the common solvent. In other words, all components must be capable of dissolving in the solvent individually, as the solvent may display varying dispersion properties. An ideal solvent should be able to dissolve polymers with minimal intermolecular interactions. Due to the large hydrogen bonding network and resulting high crystallinity of cellulose, it is difficult to dissolve in typical organic and aqueous solvents and thus, disruption and breaking of these bonding can be done by the specific solvent (Mohd *et al.*, 2017). The degree of dispersion of the combined solution is an additional crucial factor for achieving high conductivity and a solid mechanical structure in composite films. It is challenging to establish a well-dispersed morphology of conductive materials on a nanocellulose substrate (Hsu and Zhong, 2019).

The effect of the ratio of polymer to conductive filler on electrical conductivity has been investigated by Tominaga *et al.,* (2020) , that suggest the ratio of conductive filler to CNF may not have a significant effect on the electrical conductivity of thin films (Tominaga *et al.*, 2020). In their research, various ratios of MWCNT/CNF were prepared and their resistance was evaluated to assess the film's conductivity. Instead, they agreed that the degree of dispersion should be the primary determinant of thin film conductivity performance. Even if it appears well-mixed to the naked eye, this is not the case on a microscopic scale. Through cyclic voltammetry, a MWCNT/CNT film with a resistance of 200 ohmcm^{-1} was evaluated as an electrode. The graph of voltametric response looks to have a decent curve, suggesting the presence of a redox reaction and the electrode's eligibility for application. Interestingly, the thin coating did not dissolve even after a week of immersion in the solution, demonstrating its longevity in application.

CHAPTER 3 METHODOLOGY

3.1 Research Methodology

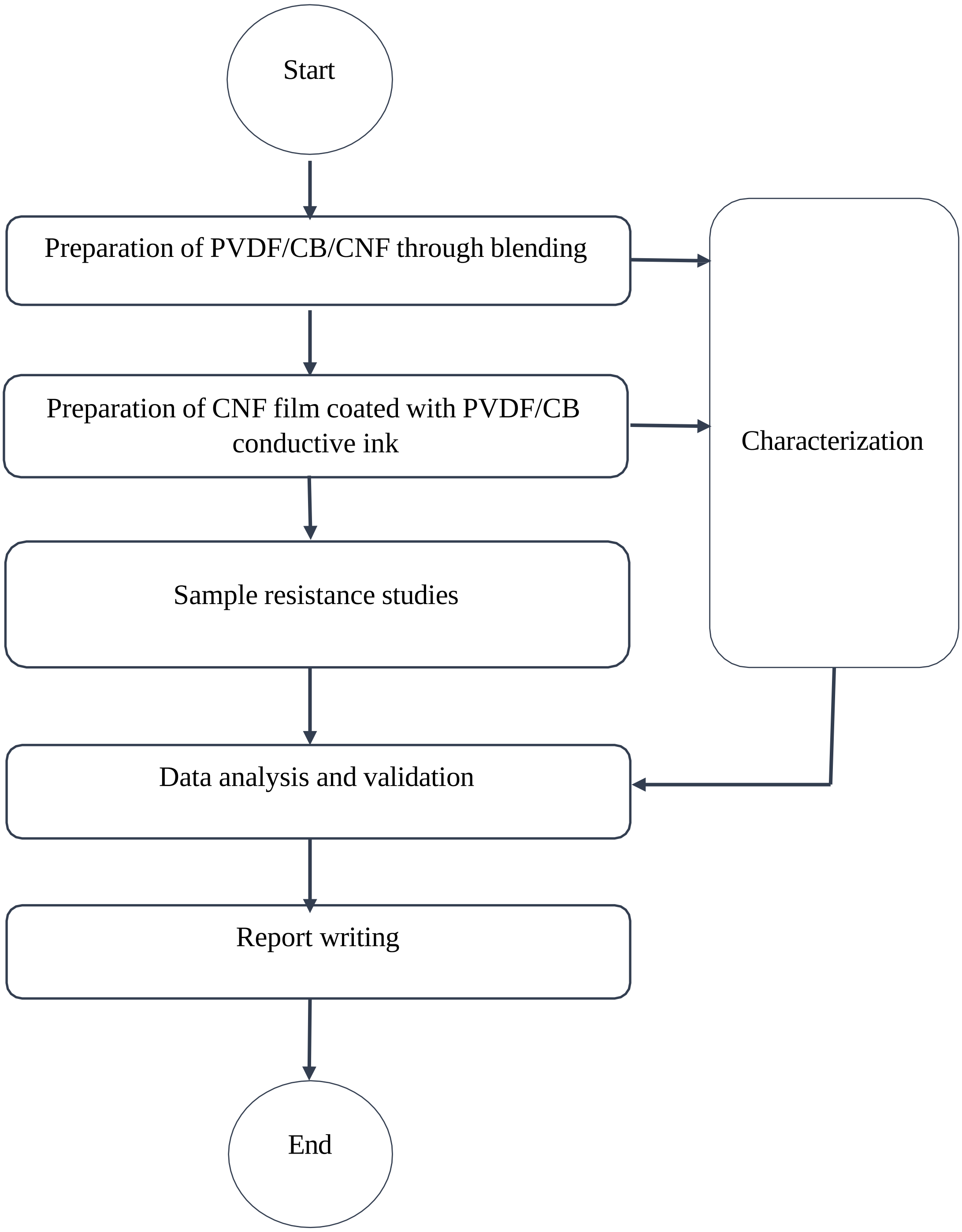

Figure 6 Flow diagram on research project for fabrication of nanocellulose-based conductive film for electrochemical applications

3.1 Materials

All chemicals were used without further purification. The hydrophobic polymer, polyvinylidene fluoride (PVDF) (Solef® PVDF) was dissolved in N-methyl-2-pyrolidone (NMP) (>99.5%) solvent. Non-solvent additives, lithium chloride (LiCl) was used to obtained LiCl-DMAc solvent system for dissolution of CNF. Cellulose nanofiber (Exilva F01-V, 10 wt.%) with the length up to 100 μm and diameter at 10−100 nm was sponsored by Borregaard Cellulose Fibrils in Norway. For conductive filler, carbon black (CB) was used which was supplied by the School of Material Engineering. Potassium Hydroxide (KOH) will be used for voltammetry characterization of the thin film.

3.2 Synthesis and fabrication of PVDF/CB/CNF conductive film

The synthetization and fabrication of conductive thin film were carried out based on two methods; blending and coating on PVDF/CB conductive ink. The composition ratio of all samples are presented in table of each section.

3.2.1 Preparation of PVDF/CB/CNF conductive ink

In this present work, an easily operated method was used to prepare the CB/PVDF/CNF composite films at a modest temperature. Firstly, the PVDF was dissolved in DMAc solvent according to the desired solid mass ratio of PVDF and CB. For instance, a total of 1 g of solid mass was set to produce a 4:6 solid mass ratio of PVDF/CB. The mass of 0.4 g of PVDF was dissolved in DMAc solvent on the mechanical heating stirrer at a temperature of 55℃ and 200 rpm. CB with a mass of

0.6 g was sonicated first for 30 minutes using at 50 Hz. After PVDF has been dissolved (clear solution obtained), CB was then mixed with the PVDF and the stirring continues for 3 hours until a homogenous viscous solution is obtained, known as the conductive ink.

3.2.2 Synthesis of PVDF/CB/CNF through blending method

For the blending method, there is an addition of CNF before the CB was added. While PVDF was being dissolved in DMAc solvent, CNF was dissolved separately in the common solvent. A total mass of 0.5 g consisting of PVDF and CB was measured with the selected ration of 6:4. Five films were prepared with an addition of CNF of different weight percent of the total dry mass of PVDF and CB (10, 20, 30, 40 and 50 wt%). As an example, to make 10 wt% CNF, 0.05 g of CNF was added to 5 drops of DMAc with continuous stirring at room temperature for 3 hours. Meanwhile, 0.2 g of PVDF was dissolved separately in 3 ml of DMAc with continuous stirring at 55 C until the solution turned clear. CNF was then added into the PVDF slurry and stirred for 2 hours before adding 0.3 g of CB. The mixture was stirred for another 2 hours.

The slurry mixture was cast onto the square glass. To get an even thickness, the slurry conductive mixture was spread with a hand cast membrane tool using a film coater machine (XB320D). The glass was put in an oven to allow the evaporation of the DMAc solvent for one day.

On the next day, the slurry mixture that had now turned into thin film was peeled off the glass. Then, the film was cut to a standard size to obtain a consistent measurement. The composition of materials in the prepared sample are listed in **Table 1**.

Table 1 Conductive film prepared with their composition through blending

Sample	**Composition (Ratio by dry weight)**		
	PVDF	CB	CNF
PVDF/CB/CNF1	6	4	1
PVDF/CB/CNF2	6	4	2
PVDF/CB/CNF3	6	4	3
PVDF/CB/CNF4	6	4	4
PVDF/CB/CNF5	6	4	5

3.2.3 Synthesis of PVDF/CB/CNF film through coating on CNF film

Through the coating method, the effect of LiCl during the preparation of CNF film and the effect of carbon loading were studied. The same procedure was followed for the coating method to achieve the conductive ink. The CNF film, which serves as a substrate instead of non-woven cloth, was prepared separately with different concentrations of LiCl (0, 5, 10, 15, 20 wt%). A LiCl-DMAc solvent system was prepared in advance with a total amount of 3 ml. Accordingly, 5 wt% of LiCl, which is equivalent to 300 mg, was added to 3 ml of DMAc while stirring at room temperature until fully dissolved. The solution should turn colourless, indicating that there is no LiCl in solid form.

The preparation of the CNF substrate was done through the dissolution of 10wt% CNF (as given by the supplier) in 10 ml of DMAc along with the prepared LiCl solution previously with varied concentration. A total of 1 g of CNF is added into the