warwick.ac.uk/lib-publications

Applications for Conductive Polymer in the Electrical Industry

Innovation Report

Wai Kam Chung

Submitted in partial fulfilment of the requirements for the degree

of Doctor of Engineering (EngD)

WMG, University of Warwick

April 2019

DECLARATION

I hereby declare that I am the sole author of this Innovation Report. The integration and the design of how innovation was applied within the study was undertaken by myself with all subsequent analysis and new knowledge generated as a result of this study being my own. This work has not been previously submitted for any other academic degree or qualification.

<div align="center">

Wai Kam Chung

24 April 2019

</div>

EXECUTIVE SUMMARY

Corona and partial discharges affect a number of different segments of the electrical industry, such as the economic impact on downtime cost and the disruption to people's daily activities. Many products are available in the market place such as semi-conducting paints or wrapping tapes, however each has disadvantages in application.

X-Fiper are one of three manufacturers in the world producing meta-aramid paper for the electrical insulation industry and wish to investigate a solution for corona protection. Therefore the aim of this research was to develop and deploy a new product solution using the X-Fiper process to resolve the aging issue caused by high voltage peaks. Conductive polymer was selected to integrate with insulation polymer to potentially enhance the capability of diverting the high energies pulses and protect the windings and wall insulation. With an aim to create materials to act as an electrical insulation material (EIM) to both insulate and absorb high energy impulses; and be conductive and re-direct the high energy impulses. The innovative material is to be used in conductor wrapping application. A stage gate new product development plan was implemented to carry out this project.

From a literature review, PEDOT:PSS was selected as the best candidate conductive material for this research. There are five paper making process stages at X-Fiper, which were all investigated for their ability to integrate PEDOT:PSS into production. The five process stages were meta-aramid polymer solution, in fiber, in fibrid, base paper and the final calendered paper. The results show that PEDOT:PSS and meta-aramid could be mixed in polymer solution, but separated after 24 hours if not agitated. In fibrid films and fiber, the PEDOT:PSS could not be retained due to the washing processes. The base paper, when integrated with PEDOT:PSS showed enhanced conductivity. When calendered, the conductivity was enhanced. This process has been taken on to production trials. The optical microscopy from prototypes evidenced that the integration of PEDOT has shown no significant impact on structure of the paper. This research has confirmed and expanded the uses of ICP as integrated PEDOT:PSS on meta-aramid paper. The optimization of aqueous PEDOT:PSS needed in this project has been designed as 1% w.t. solid content and the confirmation of process mechanism to increase conductivity can be achieved by additional layers of coating or by increasing the PEDOT:PSS solid content. Conductive meta-aramid paper offers a price competitive solution and freedom from metal particle or carbon black in the electrical industry. Customers have validated the prototype screening in terms of paper properties and are prepared to go for next stage of material qualification in their application trials and industrial qualification. Further work is required to develop the process for large scale manufacture to ensure coating uniformity and conductivity.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

The list below contains some of the commonly used abbreviations found within this report.

°C	Degrees Celsius
AC	Alternating Current
CNF	Cellulose Nanofibre
CPs	Conductive Polymers
CR	Corona Resistant
DEFMA	Desig Failure Mode Effects Analysis
DMAc	Dimethylacetamide
DSC	Differential Scanning Calorimeter
ECPs	Extrinsically Conductive Polymers
EIM	Electrical Insulation Materials
EMI	Electromagnetic Interference
EngD	Engineering Doctor
FTIR	Fourier Transfer Infrared Spectroscopy
GDP	Gross Domestic Product
ICPs	Intrinsically Conductive Polymers
ITO	Indium Tin Oxide
LOI	Limiting Oxygen Index
MPE	Modified Polyester
NEMA	National Electrical Manufacturers Association
NMP	N-methyl pyrrolidone
PA6	Polyamide
PAI	Polyamideimide
PANi	Polyaniline
PD	Partial Discharges
PEC	Polyelectrolyte Complex
PEDOT	Poly(3-4-ethylene dioxythiophene)
PEN	Polyethylene Naphthalate
PET	Polyethylene Terephthalate
PI	Polyimide
Ppy	Polypyrrole
PSS	Poly(styrenesulfonic acid)
PWM-VSCs	Pulse-width-modulated Voltage-source Converters

REACH	Registration, Evaluation, Authorization, and Restriction of Chemicals
RoHS	Restriction of Hazardous Substances
SOPs	Standard Operating Procedures
TGA	Thermogravimetric Analysis
UL	Underwriter Laboratories
VPP	Vapor Phase Polymerization
VSCs	Voltage Source Converters

CHAPTER I – INTRODUCTION

1.1 Electrical Insulation Material (EIM) Damage and its Causes

In the electrical industry, in large rotating electrical machines, a large voltage of around six to ten kilovolts is almost always applied between a coil portion that is a conductor and a slot or turn insulation material that is an insulator. When electrical partial discharges (PD) occur in this portion, the insulation is damaged by ionized molecules, so that the lifetime of the rotating electrical machine is greatly shortened. In addition, when the thickness of the insulation layer is reduced, such as with the recent miniaturization of devices, the electric field intensity increases, and the possibility of such PD tends to increase (Fujimori 2014). Furthermore, the increasing availability of reliable and efficient power electronics has created a transition to driving AC induction motors with pulse-width-modulated voltage-source converters (PWM-VSCs). Voltage source converters (VSCs) can create thousands of short rise-time voltage surges per second. Such surges may lead to more rapid aging of the insulation. These surges and PD may gradually erode the insulation both between turns and within the main wall insulation (the material to prevent a ground fault occurring from high potential in insulation in a high voltage rotating machine) (Shakweh 2018, pp.936-937). Figure 1 shows the location of main/ground wall. PD occurs not only in a motor with PWM-VSCs and high voltage rotating machine but also in high voltage transformers.

Rotating Machine - Form Coil

A) Conductor or conductor coating

B) Conductor insulation

C) Stack consolidation materials

D) *Main wall insulation & Turn Insulation & Slot insulation*

E) Finishing or sealing tapes or end-winding

F) Corona protection (location of bar to bar)

G) Bracing materials

H) Impregnating resin

I) Slot wedging materials
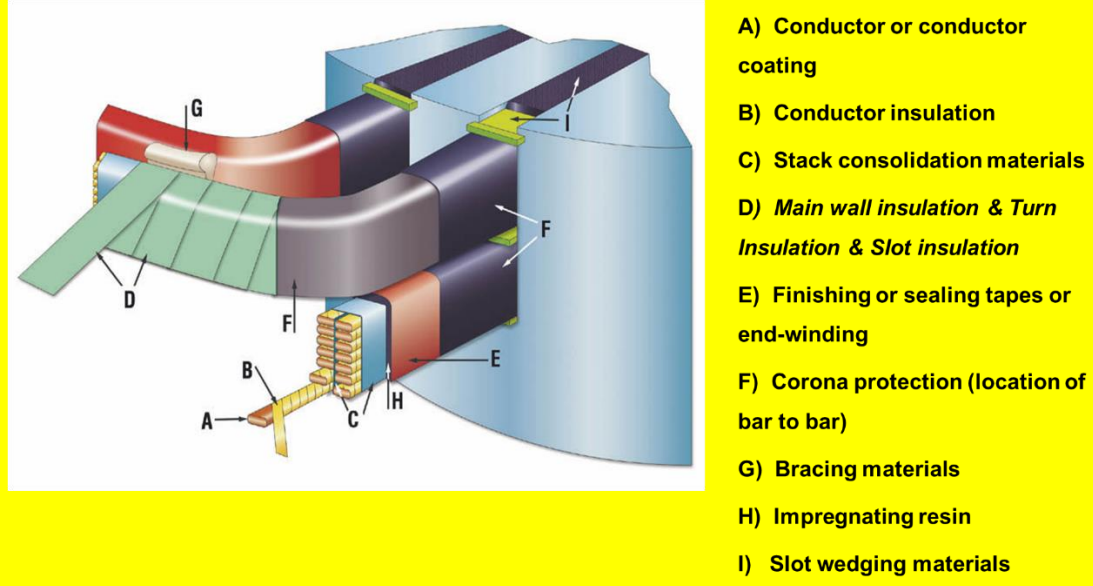
Figure 1: The location of "Main Wall Insulation" and the "Turn Insulation" in a high voltage Form-wound insulated coil as standard in high voltage motors and generators adapted from Von Roll High Voltage Training Material, (2012).

1.1.1 Pulse Width Modulation (PWM)

VSCs of the PWM type are commonly used in various motor applications such as three phase alternating current (AC) motors. The rapid acceptance of variable speed technology has been due to the energy savings associated with running the rotor (a part of motor) at a lower speed when feasible. The short rise time pulses (voltage surges) are caused by a PMW converters voltage source, which has been identified as a cause of stator winding insulation failure in low voltage motors for more than 25 years (Stone *et al*., 2007). The root cause was found to be the large number of PWM voltage pulses from the drive, which caused PD between turns in the stator. These discharges eroded the magnet wire insulation also known as round enamelled conductors (Figure 2), which finally results in insulation and motor failure. In medium voltage machines the converter surges will also increase the stator winding temperature due to both (i) dielectric heating of the ground wall insulation and (ii) heating of the stress control

coatings.   In addition, the surges may cause an increase in PD activity, both between turns and within the ground wall insulation.

Rotating Machine - Random Coil

Typical induction motor stator section terms and materials.

Cable
Connection Tape
Wedge
Lead Sleeving
Slot Separator
Tie Cord
Phase Separator
Coil Nose Tape
Turn Insulation
Slot Liner
Bracing

Insulation Material
- **Round Enameled Conductors/Magnet Wire**
- **Flexible Laminates**
- **Support and Bracing materials**
- **PSA Tapes**
- **Lead Wires**
- **Vanishes and Resins**
- **Specialty Topcoats**

Figure 2: Rotating machine for random coil adapted from Von Roll High Voltage Training Material, (2012).

1.1.2   High Voltage Rotating Machine - Motor & Generator

Most failures on high voltage rotating machines are electrical in nature.   For example, the mechanical problem of wedge looseness will eventually cause the erosion of conductive coating.   The PD will affect a phase-to-ground or phase-to-phase insulation resulting in failure.   The other types of discharge sources are:

- End-winding defects which come from surface tracking, bar-to-bar discharges and corona discharge at the junction of the field grading system.
- Slot discharge activity, occurring between the slot section and the steel core surface.
- Internal discharges, occurring within the ground-wall insulation when the voltage is over 6.0 KV for rotating machine insulation.

- PD sources from delamination in the ground-wall insulation at the copper conductor (Judon *et al.,* 2005).

1.1.3   High Voltage Transformer

This problem is not limited to the motor/generator industry; it also occurs in the transformer industry.   Soomro and Baharom (2013, p.13) states that PD is one of the main causes of deterioration of insulating material in power transformer windings. Figure 3 exhibits the causes of PD occurring of in power transformers that internal discharge, surface discharge, corona discharge and electrical trees (electrical networks). Furthermore, transformers in electrical networks can be exposed to over-voltages with a wide range of frequencies.   Such over-voltage can occur during the opening and closing of a switching device, the re-strikes and pre-strikes produce high frequency over-voltage that become a major problem of transformers failures.   Both increased impulses transients and harmonic content cause unstable power quality (Bahadoorsingh *et al.,* 2007).

Causes of PD occurrence in power transformer
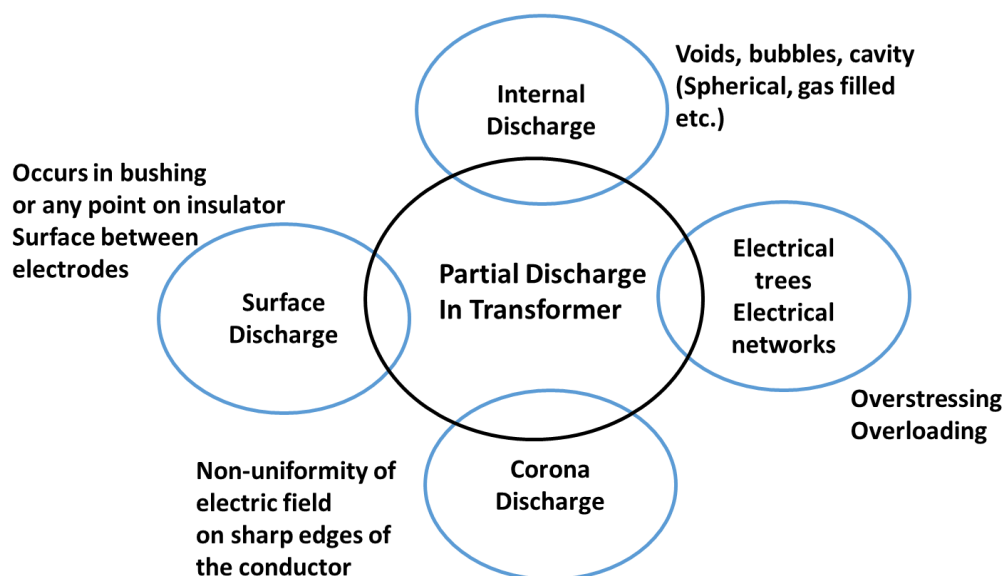
Figure 3: Causes of PD occurrence of in power transformer adapted from Bahadoorsingh *et al.,* (2007).

4

In fact, the problem is connected to all applications such as motors, transformers and other electrical components which are switching to high frequency electrical signals as the power supply. The high impulse issues affect different segments of the electrical industry by design and result in the high energy spikes which originate inside of electronic/electrical devices.

1.1.4 The Mechanism of PD

Corona and PD are phenomenon caused by the ionisation of gas molecules in a strong electric field. The radicals or ions generated in corona reactions or PD rapidly destroy organic materials in low, medium and high voltage insulation machines. Figure 4 exhibits how the ionisation occurs and destroys insulation materials. PD only occurs where there is a gas between the two conductors. Negative electrons move through air toward the positive charge. When the electrons hit the edge of the void, any organic material will be gradually decomposed (Stone, 2014, p.21).

Figure 4: Mechanism of PD , drawing adapted from Von Roll High Voltage Training Material, (2012).

1.2 Industrial Importance

It has been shown that the high impulse problem relates to different segments of the electrical industry. This is a challenge to provide the total value of the impact if the products/equipment/components fail due to this high impulse problem.   While specific total values are not possible, it is possible to give a rough idea of the magnitude of the problems generated and expressed in the way that it affects our daily life. Products such as home appliances, telecommunications products, office equipment, automobiles, public transportation, and power supply equipment/components made by electrical industries are used in houses, offices, factories, schools and hospitals as part of people's daily activities.   The volume of household, commercial and industrial uses of electrical and electronic products and parts is enormous; for example, Renmin (2006) states that the global electronic hardware production in 2005 was US$1,430 billion which is almost 5% of the World's gross domestic product (GDP) with annual growth of 5 to 7%. Furthermore, Penrose (2000) discusses the financial impact of motor failure in a segment of the total market - the motor industries in United States where there are 1.2 billion electric motors of all types, and the downtime cost is 200,000 USD/hour (Table 1).   A recent study from Immerman (2018) in his article "The Real Cost of Downtime in Manufacturing" indicates that when unplanned downtime occurs, no value is being produced but the cost of overhead operations continues to grow, which directly impacts a company's bottom line. Furthermore, 82 percent of companies have experienced unplanned downtime over the past three years and that unplanned downtime can cost a company as much as $260,000 an hour.

Table 1: Down-Time cost when motor fails (Penrose, 2000)

Industries	Downtime Cost USD/hour
Forest Products	7,000
Food Processing	30,000
Petroleum and Chemical	87,000
Metal Casting	100,000
Automotive	200,000

High impulse problems are one of the failure mechanisms affecting the insulation properties on winding. The other causes of failures are the aging mechanisms, working environment, and related property changes. According to a research study by Thorsen and Daiva (2007), covering 3,720 machines from 5 to 15 KV for medium and high voltage electrical devices, at least 20% of failures were related to insulation breakdown. One of the major cause of insulation breakdown was correlated to winding insulation. A recent survey (Christina *et al*., 2017) identified the cause of transformer failures and indicated almost 34% of the total causes of component failure in service was related to the winding. To avoid the cost of downtime and to enjoy effective and efficient daily activities, reliable electrical and electronic products for various applications are required. Thus, it is necessary to develop an electrical insulation system or a product that is capable of relaxing an electric field generated between a coil and an insulation material in order to reduce the generation of corona. This is the focus of this EngD work.

1.3 Existing Solutions and Challenges

1.3.1   Form Coil – Wrapping Wire Conductor

The corona protection system acts to minimize internal coil PD activity; refer to the Figure 1.   For an electrical rotating machine, the insulation is provided by insulation materials put on conductor wire for turn-to-turn insulation, slot and phase for ground insulation and/or main wall insulation between the conductor and the core steel.   The most common way of applying the electrical insulation is to use layers of a conductive thin sheet material.   Examples of Electrical Insulation Material (EIM) and details can be found in Submission II Section 3.3.3 and are materials such as polymers: Polyethylene terephthalate (PET) film, Polyethylene naphthalate (PEN) film, Polyimide (PI) film. Others are fibrous paper such as cellulosic paper (wood) and meta-aramid paper (synthetic), mica paper, etc. that are wrapped (Van Vooren 2012).   The conductive or semi-conductive wrapping materials for corona protection are mainly used for wrapping the conductor to improve the turns/winding insulation and the corona resistance in the areas when the coil exits the steel core stack.

For instance, in a 6.6 KV high voltage rotating machine, conductive and semi-conductive mica tapes can be used for corona resistant or PD protection (See F in Figure 1).   Such conductive or semi-conductor tape is made by the combination of insulation materials of mica, polyester fleece and conductive material most commonly made of carbon particles. This construction can help to relax voltage stress and suppress PD at the core. Carbon black is not suitable for use or application in clean environments and sensitive areas because of the possibility of contamination.   Thus, the main drawback of carbon particles in the conductive or semi-conductive mica tapes is its intrinsic black colour and the tendency to release conductive particles that dissipate in the clean room air and may cause undesired shorts (Ghani *et al.,* 2010).   In addition, the carbon particles are easily released from the mica tapes during the process of winding and

8

process of resin impregnation. Such released conductive particles become the contamination in an electrical insulation system that reduces heat transfer and leads to electrical tracking failure. Furthermore, DuPont™ meta-aramid with carbon black also has a very expensive comparative selling price, making market penetration difficult. Therefore, while presently used, these types of conductive or semi-conductive tapes are unable to resolve the problem of insulation degradation caused by a high voltage pulse. Industry requires a new conductive or semi-conductive tape that can resolve the problem of released conductive filler during the winding and process of resin impregnation.

1.3.2   Random Coil – Wire Enamel Conductor Wire

For medium and low voltage rotating machine, Rea Magnet Wire Company Inc. (Rea Magnet Wire n.d), had introduced corona-resistant wire enamels coated conductor (Figure 2 exhibits the location of wire enamels conductor that provides the capability of improving lifetime with respect to the application of surge voltage of an inverter and thermal degradation). Rea Magnet Wire (Quantumshield) uses MW 35 (Magnet wire with National Electrical Manufacturers Association (NEMA) standard of MW35 - can withstand thermal aging of 200°C) for inverter applications. This is a two-layer construction with a conductive layer inserted between the two insulating layers over the conductor. This is, making a coaxial cable on the scale of magnet wire. e.g. EIM/conductive layer/EIM. The inorganic filler material, which is actually a conductor in the form of fine flat particles, allocates a conductive pathway to dissipate the electrical energy between the two intended layers of isolation materials around the electrically conductive wire (Hirai 2003). This approach works only to a limited degree because of the increase of stiffness and tensile properties. The conductive layer was always a problem – die wear, uniformity of application and other aspects resulted in limited success. This co-axial construction of the magnet wire insulation is

expected to be applied in thin layers because the thin layers offer flexibility to the applied insulation.   The above technology by adding a conductive layer between two layers of insulation did not provide enough overall protection to resolve the problem of high energy surge voltage spikes. The challenges would be the ratio between the content of the conductive layer and the conductivity.   Therefore, it is still a need for industry to have corona protection of wire enamel coating.

Wire enamel coating manufacturers such as Elantas (one of the largest wire enamel makers in the world) (Elantas 2018) and Herberts (Herberts 2000) have developed corona-resistant wire enamel coatings that manufacturers could take advantage of when making corona-resistant wire. Usually, corona-resistant insulated wire is made by three layers of insulation coating.   The outer layer is the wire enamel of Polyamideimide (PAI); the middle is a corona resistant enamel (CR) and the inner layer is a modified polyester (MPE), as shown in Figure 5.   In BCwire® for example, the construction is MPE/CR/PAI CORONA-R®. According to Choi *et al.,* (2006), an experimental endurance test was done between The Hong Kong Polytechnic University and P. Leo & Co., (B.C.) Ltd., for the copper insulated by 3 layers of MPE/CR/PAI that is namely BCwire® and confirmed that the endurance is greater as compared to the conventional single and double insulation wire.   However, it is the author's unproven assertion founded through industrial experience that it is impossible to eliminate the voids in electrical systems totally no matter how many control processes have been implemented as the degradation of insulation materials creates voids in the insulation system.
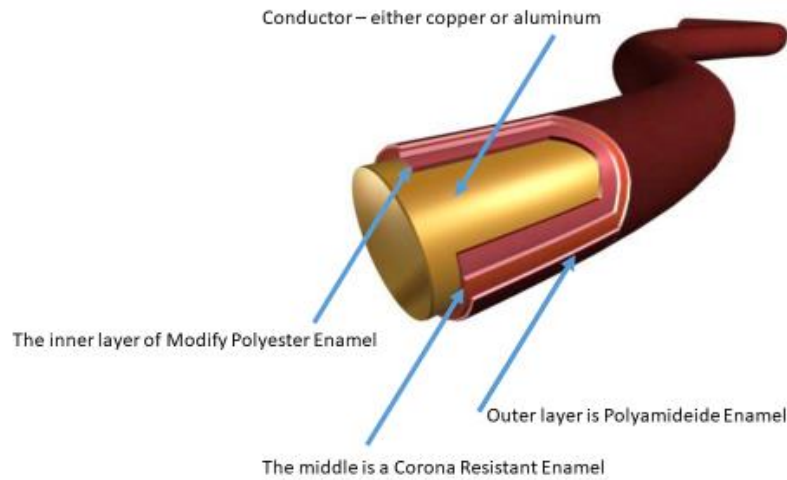
Figure 5: Configuration of the BCwire® with 3 insulation layers MPE/CR/PA (Choi *et al.,* 2006).

1.4 Research Objectives

The previous approaches have been so limited that electrical insulation manufacturers are trying to find an entirely different solution in the electrical insulating side.   The failures to find the needed solution is due to the previous approaches which in fact consist of trying to solve a complex problem by focusing on only one aspect of the total electromagnetic energy system to absorb the energy.   To absorb a high amount of energy requires more than the EIM alone, such as the magnet wire approach provides. A very significant part of the absorption of the high energy voltage spike solution is the inclusion of the magnetic characteristic; a natural component of electrical energy is electromagnetic.   To absorb these high energy pulses, magnetism as a major absorbing component is required.

One of the recent approaches in attempting to overcome some of these limitations is to develop composites of both conducting polymers with non-conducting polymers to improve mechanical performance and electrical conductivity.   Further, the current

11

solutions of conductive and semi-conductive tape for high voltage form-wound coil and corona resistance wire enamel for random coil are insufficient to resolve the corona or PD issues. Therefore, the aim of this EngD. program is to provide a solution to fill the gap by building a product instead of developing or modifying a single material or component to revolve PD or corona issues caused by high voltage peaks. To help the insulation system to absorb these high energy pulses, magnetism as a major absorbing component is required. Other than carbon black and metal particles, the conductive material of conductive polymer will be examined to be considered to be used as conductive or semi-conductive tape for corona protection.

The aim of this innovation is to combine a spectrum of conductive and insulating polymer materials, to develop a multifunctional system such that:

1. Polymeric materials provide the electrical insulating material
2. Polymeric materials provide the conductive material and absorb, re-direct and conduct high energy pulses safely out of the equipment

1.5 Scope

The potential intrinsically conducting polymers available in the market or laboratory were evaluated and selected to be used in this project. It was necessary to find compounds that are stable under ambient conditions and easily-processed. The scope of the Innovation Report rests solely on the design, structure and materials that can be used as corona protection to absorb high energy impulses, be conductive and re-direct the high energy impulses as corona protection material for the wrapping the conductor wire in form coil. Enamel coating conductive wire will not be studied here.

Development and modification of new Conductive Polymers (CPs) will not be within the scope of this project. Only film and paper forms of EIM are discussed. Other insulation materials such as varnish, resin, tubing, and bobbin, etc., will not be covered and are considered out of scope. It is noted it might not be possible to exhibit how to totally replace conductors by using conductive polymer.

X-Fiper New Material Co., Ltd. and Eltek Laboratory Inc. are the sponsor companies to this EngD project. This report has been produced utilising many resources both internal and external to the sponsor company. The experimental resources of hardware (materials and equipment) and software (human resources, financial funding, product know how, technique know-how, and process know-how), are provided by the author's company in the form of purchasing, production, research and development, quality control and laboratory facilities across various departments. The conductive polymer supplier provided an engineer and product development team. Various motor and transformer manufacturers also contributed. X-Fiper is a young manufacturing company which does not have comprehensive research and development process and testing equipment. This becomes a limitation in terms of financial support for additional testing needed to be done externally.

1.6 Research Methodology of EngD Portfolio

The research methodology is illustrated in Figure 6 and consists of five phases covered by submissions. Phase one and two involve the understanding the significance of the problem, need for changes, and reviewing insulation and conductive polymer areas. Phase three identifies the specification of an innovative product. Phase four accounts for specific research and development activities aligned to the aim and objectives of the project. The final phase is recognition of the commercial value of the undertaking of this innovative product. A description of each phase of the research methodology is provided in Figure 6.
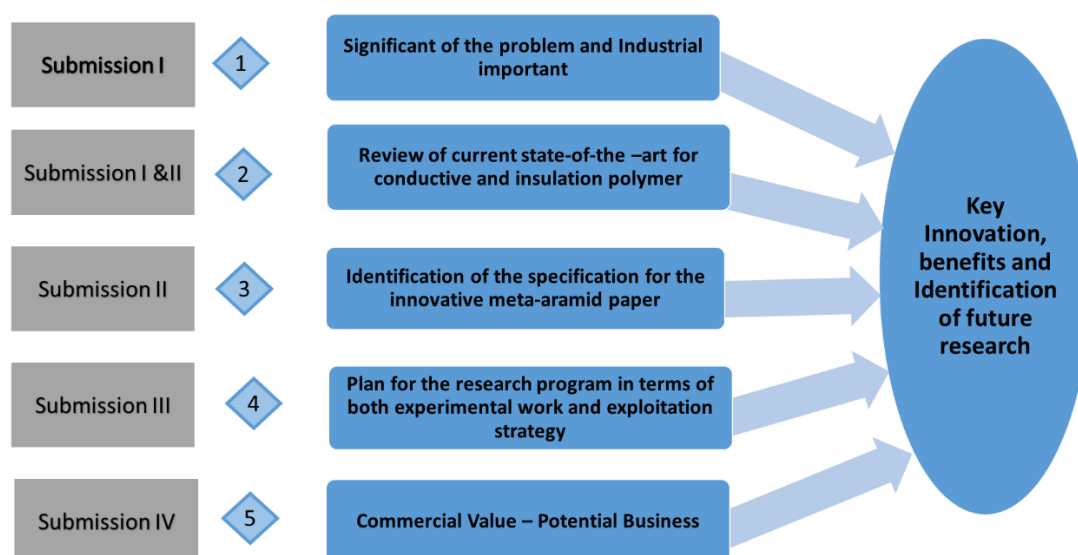
Figure 6: Methodologies /Formulation of the portfolio and expected deliverables.

While this Innovation Report overviews the entire EngD the main focus is the innovation from phases 3 and 4.

CHAPTER II – MATERIAL SELECTION

Development of all organic conductive materials (without incorporation of inorganic and metallic contents) that also have exceptional mechanical properties is a major interest of researchers throughout the world. The advantages over metals include flexibility, durability and cost effectiveness. To achieve the objectives of this EngD, a research literature review was undertaken on conductive and insulation polymer, and focused on specific industry need and product requirement in order to select materials. A summary is provided in this section.

2.1 Overview of Conductive Polymer

In this project, polymeric materials were required to provide the conductive media to absorb, re-direct and conduct high energy pulses safely out of the equipment. The review was presented in Submission I with updates covered in Section 3.3. A brief introduction to a range of conductive materials is included here for completeness.

2.1.1 Conductivity

The term conductive material usually refers to materials that have very good conduction properties including both heat and electrical conductivity, and that have a large number of conduction electrons (between one and four electrons per atom). Examples are metals such as copper, silver, iron and aluminium. The degree of conductivity is dependent on the number of charge carriers as well as the number of electrons in the material and their mobility. In a metal it is assumed that all the outer electrons are free to carry charge and when a voltage is applied across the metal, the electrons flow from one end of the conductor to the other under the influence of the electric field.

Insulating materials such as wood, glass, or ceramic on the other hand have tightly bound electrons and thus almost no electron flow activity can be found; as a result, they have high resistance to charge carriers flowing and very low conductivity. In between metals and insulators, there are materials called semi-conductors such as silicon. For these materials, the conductivity can be adjusted by changing temperature or by the loading of added charge carrying agents which are known as dopants.

2.1.2 *The Discovery of Conductive Polymers*

Polymers are used in a range of applications from containers to clothing, and are known to have good insulating properties. For example, polymers can be used to coat metal wires to prevent electric shock. Yet Alan J. Jeeger, Alan G MacDiarmid and Hideki Shirakawa changed this view with their initial discovery that a polymer, polyacetylene, could be made conductive and behave almost like a metal. (Rasmussen *et al*., 2014) This research from 1977, initiated tremendous scientific research, publications and technical results, suggesting many commercial industrial uses. In 2000, the Nobel Prize in Chemistry went to these scientists for the discovery of conductive polymers. They were successful in producing a special type of conjugated polymer which is conductive. Electrical conduction of conjugated polymers such as polyacetylene, which is by nature a semi-conductor, has low electrical conductivity at room temperature. Its conductivity may be increased by many levels of magnitude (similar to the doping of semi-conductors) to achieve conductivities comparable to those of superb conductors such as copper and silver (Ramakrishnan 2011). Figure 7 illustrates the extent to which the doping process transforms insulating polyacetylene to an excellent conductor of 10^5 S cm^{-1}, (Naarmann 2002) while copper's is 10^6 S cm^{-1}. One form of polyaniline, increases in electrical conductivity of many orders of magnitude by doping process (MacDiarmid *et al.,* 1991). For example, un-doped polyaniline

with conductivity of $10^{-10}\,\mathrm{S\,cm^{-1}}$ can be increased to $10^2\,\mathrm{S\,cm^{-1}}$ by doping. Similarity, polypyrrole doped with I_2 can increase the conductivity up to $10^2\,\mathrm{S\,cm^{-1}}$.
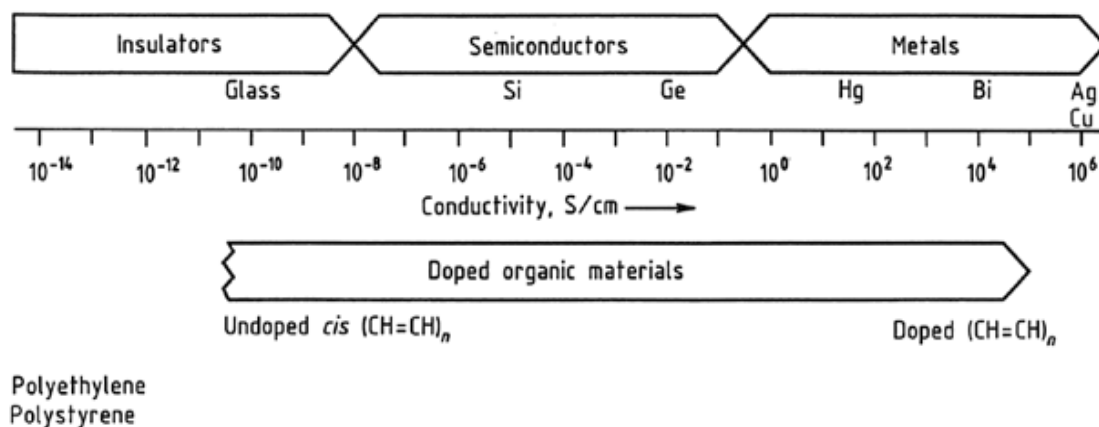
Figure 7: Electrical conductivity of organic & inorganic materials and effect of doping (Naarmann 2002).

Another dramatic move forward began when chemists and physicists began working cooperatively to invent and synthesize specific molecular structures to meet the required physical properties including the stability in synthesis, process and in use, and greater conductivity (Scott 2010; Okamoto 1985). As potential applications have been realized, scientists and researchers from different fields are participating in the evolution of conducting polymers. Electrical engineers have brought their expertise in the areas of electronics, optoelectronics and display technology. Material scientists co-working with electrochemists assessed the applications to anticorrosion coating. Bioengineers became conscious about the potential use of sensors and biomedical actuators (Smela 2003). All these collaborations have created synergy helping the understanding and development of conducting polymers.

Advance synthesis technologies such as electrochemical and/or electropolymerization and the use of nanotechnology have all helped to improve materials that are naturally conductive to increase their stability. These materials are termed Intrinsically Conductive Polymers (ICPs). Their properties can be adjusted by both initial chemical modification and subsequent processing to give the desired features. The

17

major important properties of ICPs are electrical conductivity, the ability to store an electric charge and the ability to exchange ions.   These properties have provided the potential for their use in electronics applications such as anti-static coating materials, capacitors and batteries (Elschner *et al.,* 2011, pp.9-10).   For the application of anti-static coating and batteries, ICPs can be used to substitute the metal.   ICPs have become industrial solutions when the problems are related to anti-static, conductive and electromagnetic interference (EMI) shielding.   This project is focused on conductive polymers (CPs) that can be antistatic and conductive to absorb and re-direct the high impulse out of the electrical insulation system so they are ideal candidate materials.

2.1.3   Types of Conductive Polymers

Polymers that are electrically conductive typically fall into two categories:
- Intrinsically conductive polymers (ICPs)
- Extrinsically conductive polymers (ECPs)

These types of materials will now be further defined.

A. Intrinsically Conductive Polymers (ICPs)

Polymers are molecules that form long chains, consisting of repeating units called monomers. In becoming electrically conductive, a polymer has to imitate a metal, that is, its electrons need to be free to move. There are two conditions that polymer materials must have in order to become conductive:

(i)   Conjugated Double Bonds

The major characteristic of a conductive polymer is the existence of conjugated double bonds which carry charge along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternatively single and double. Each single bond contains "sigma" (σ) bond that has a strong chemical bond and a double bond contains a comparative less strong "pi" (π) bond. Charge in intrinsically conducting polymers is transported along and between polymer molecules via generated charge carriers such as by holes and electrons. For example, the polymer of polyacetylene is prepared through polymerization of the hydrocarbon acetylene and it has the structure shown in Figure 8.
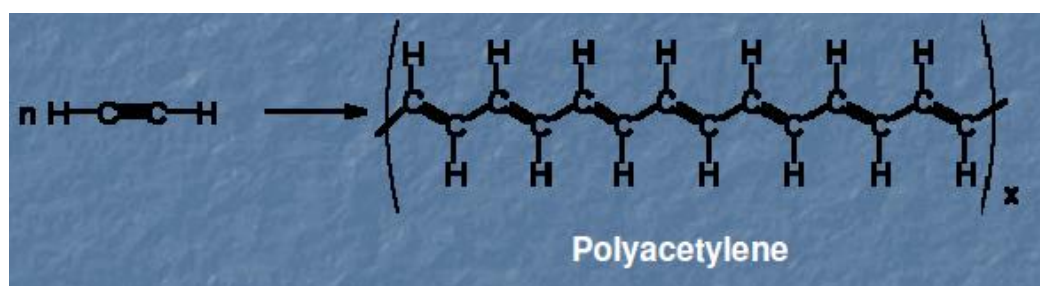
Figure 8: The Structure of Polyacetylene Conjugated Polymer (Norden *et al.,* 2000, p.2).

However, conjugation alone is not sufficient to produce the polymer with conductive property; thus, dopants are used as charge carriers in the material to provide either extra electrons or "holes" into the conjugation bond to allow the charge carriers move around (Norden *et al.,* 2000, p.2).

(ii)   Doping

As previously stated, the second condition is that the conjugated polymer chain has to be interrupted by removing or freeing electrons by the action of oxidation (p-doping) or inserting removing/free electrons with the activity of reduction (n-doping).   The process is called doping.   Figure 9 exhibits two types of doping.
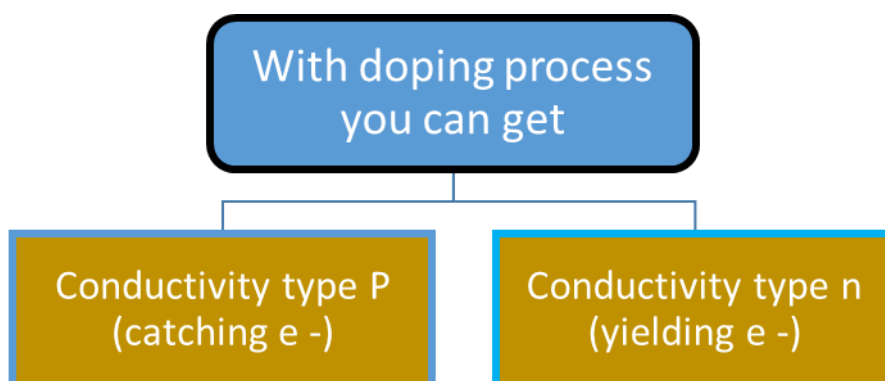
Figure 9: Two types of doping adapted from Le *et al*., (2017).

As a conductive polymer, charge transfer is needed (Schoch 1983). The doping reaction can be performed in the gas phase, in solution, or electrochemically and the reaction completes rapidly.   Besides the choices of doping materials, other factors such as the density of carriers, the mobility, impurities, the direction of conductivity either along the chain or perpendicular to the chain and temperature during the doping process are all factors affecting conductivity.   For example, impurities of 0.1 to 1% will change conductivity by 2 to 3 orders of magnitude for a conductive polymer while the impurity has comparatively little impact on metal as seen in Table 2 (Harun *et al.,* 2007). By using different types of solvents is it also possible to have some level of control over the movement of electrons within the polymer to either increase or decrease the polymer conductivity (Ramakrishnan 2011).

Table 2: Comparison of physical properties of metals, insulators and conducting polymer (Hamzah *et al.*, 2007).

Property	Conducting polymers	Metals	Insulators
Electrical Conductivity (S/cm)	$10^{-11} - 10^{3}$	$10^{-4} - 10^{6}$	$10^{-20} - 10^{-12}$
Carriers	Electrons of conjugated double bonds	Valence electrons of half-filled band	Tightly held electrons
Concentration of carriers per cm^3	$10^{12} - 10^{19}$	$10^{22} - 10^{23}$	
Effect of impurity	Impurities of 0.1 – 1 % change conductivity by 2 to 3 orders of magnitude	Effect comparatively slight	Strong effect
Magnetic Properties	Paramagnets	Ferro and diamagnets	Diamagnets

B. Extrinsically Conductive Polymers (ECPs)

As semi-conductors can be doped to vary properties such as conductivity, ECPs are also modified materials. Blends of insulating polymers with electrically conductive additives, for example containing metallic fibers or carbon in its graphite modification, are sometimes called CPs (Feast 1986). The level of conductivity will depend on the choice of additive and loading level that can be achieved from the thermoplastic compound. The main potential application of ECPs is on the development of greater resistivity to damage by static discharge for electrical and electronic products. Figure 10 is an example of preparation of conductive polymer composites using solvent mixing (Kaur *et al.,* 2015). The major disadvantage is the stiff coating layer that has the impact of lowering mechanical properties, and inferior electrical conductivity values; for example, production of conductive aramid and polyamides by coating with carbon

black, nickel-copper composite layer and supercritical carbon dioxide has been reported (Zxou *et al.,* 2013, pp 453-458; Zhao *et al.*, 2006).
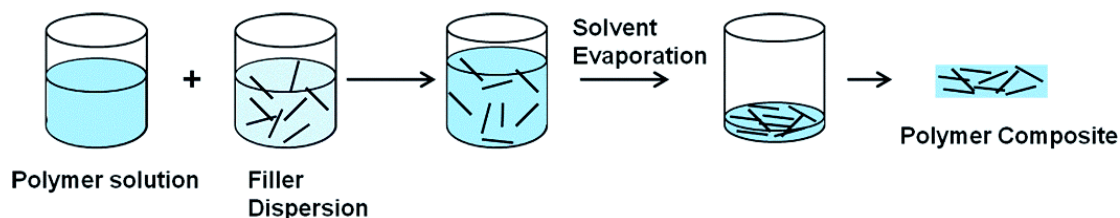
Figure 10: Example of preparation of conductive polymer composites using solvent mixing (Kaur *et al.,* 2015).

C. Current Applications

There are advantages in considering conductive polymer compared to metal materials: they can be economically fabricated into complex shapes, and are ideal for use in products where space and weight considerations are critical to provide weight-reducing potential.   The electrical properties can also be fine-tuned using the method of organic synthesis such as to control the type and volume of solvents which can affect the polymer's electrical charges and finally increase its conductivity.   CPs are increasingly used for a growing number of complex applications (Naarmann 2002). The following are the main applications: (Amarasekera 2005)

- o Dissipative ("anti-static" polymers)
- o Conductive (materials competent of conducting medium amounts of electrical current)
- o Highly conductive or shielding (materials capable of conducting major amounts of electrical current)

In relation to the aim of this project it can be seen that by modifying the doping formulation and process, it is possible that a conductive polymer could achieve

conducting a current and diverting the unneeded static electricity from the electronic component or product to avoid electrical damage. Identifying the specification or function required for the corona or partial discharge protection purpose materials can therefore be considered a realistic research focus. Once specifications are recognized, appropriate materials can be selected and the processes can be optimized.

2.2 Electrical Insulating Polymeric Materials: Meta-aramid paper

2.2.1 Introduction

Since X-Fiper focus on the production of meta-aramid products, this Innovation Report will focus on this material as the choice of electrically insulating material. Details of other candidate materials can be found in Submission II Chapter 3.

Meta-aramid paper is made from short length fibers called floc and small binder particles called fibrids. (Yao *et al.,* 2013). These meta-aramid materials, in the shape of floc, and fibrids are formed into a sheet structure on a Fourdrinier paper machine without the use of additional adhesives, binders, fillers, or any type of additive. The products are then calendered to densify it to a desired specific gravity (density) of 0.7 to 1.2 (depending on the required thickness). Further details of the meta-aramid production process was covered in Submission II Chapter 5.

2.2.2 Meta-aramid: Property Requirement for High Voltage Application as Conductor Wrapping Tape in this Project

In comparison to materials such as polyester film, meta-aramid paper has better thermal resistance and impregnation properties and effectively absorbs the resin (Submission II

23

Section 3.4 c). The resin is well adhered to the surface compared with polyester surfaces that are glossy and nonporous (Pyrhonen *et al.,* 2008).   Figure 11 shows a list of some key advantageous properties for meta-aramid, some of relevance to this application will now be more fully described.

Meta-aramid due to their chemical structure and high crystallinity, meta-aramid have remarkable physical, thermal, mechanical properties, etc., compared to industry standard measure

Key Properties for Project Needs

Advantages:
- High Temperature Resistance
- Flame Retardant
- High Mechanical Strength
- High Chemical Compatibility
- Low Thermal Shrinkage
- High Ultraviolet Resistance
- Non-toxicity
- Moisture Resistant

Potential disadvantages:
- Low Dielectric Strength
- Low Elongation to Break
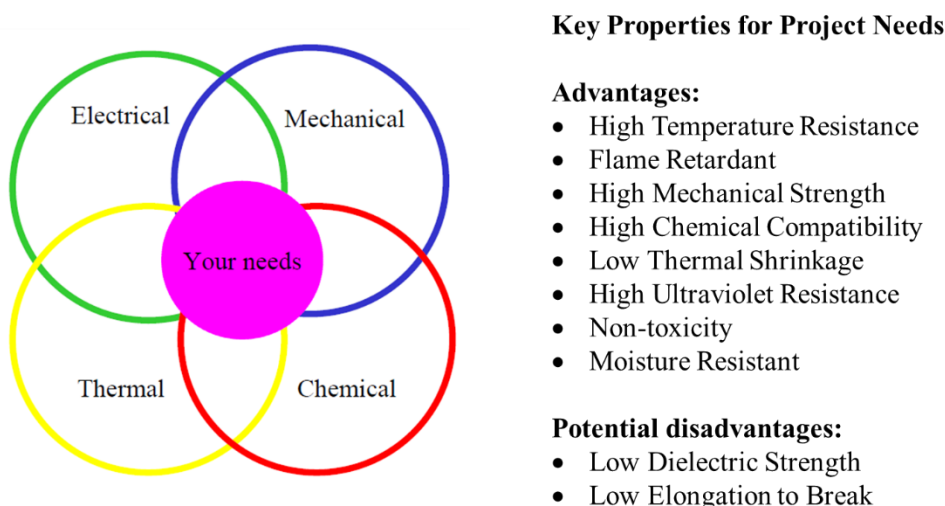
Figure 11: Key Properties for meta-aramid paper.

i)   High Temperature Resistance

Electrical applications for high voltage transformer, motor and especially compact size electronic equipment, require temperature resistances greater than 180 ºC and should be both flame retardant and not be readily combustible. Meta-aramid heat resistant insulating paper is mainly composed of the polyisophthaloyl metaphenylene diamine fiber (Aramid 2001).   The key property of high temperature resistant paper is their continuous operating temperature.   At the temperature of 220ºC meta-aramid paper will still retain the electrical and mechanical properties for a long period of time. Commercial products are available from the manufacturers DuPont™ and X-FIPER, and will withstand UL 746B thermal aging index (UL 746B Standard, 1988) for

24

example: DuPont™ type 410 Paper will maintain 300 volts/mil (12kV/mm) (Material Data Sheet Nomex®) and X-FIPER type X-630 will retain 250 volts/mil (10kV/mm) (X-Fiper® data sheet) and dielectric strength for several hours at around 400 and 350°C respectively.

ii) Flame Retardant

Certified flame retardants materials were obtained based upon the Underwriters Laboratory testing standard of UL94 (UL 94 Standard 1988).   Flame retardants, refers to materials that could inhibit, suppress, or delay the production of flames to prevent the spread of fire.   Meta-aramid paper made by DuPont™ or X-FIPER both obtained UL 94 flame retardant certification.   Flame retardant capability is normally measured by the limiting oxygen index (LOI), the amount of oxygen level needed in the atmosphere to support the combustion. Meta-aramid has (LOI) greater than 25; thus, there must be at least 25% oxygen present in order for them to burn (Smith 1999). This is the standard that must be achieved by any new product.

iii) Mechanical Strength

A calendered meta-aramid paper is smooth with good wear resistance, high tensile strength and tear strength, and easy for processing or shaping.   Increasing the moisture content up to 7% (normally, moisture content is 3-5%), has limited impact on the dimension but has improvement on the mechanical properties of elongation, toughness, fold endurance, impact and tear strength.   (Material Data Sheet Nomex® data sheet).

iv) Chemical Compatibility

Meta-aramid paper products remain stable in most common solvents and have extreme resistance to corrosion by acids, alkalis and ketones (Supriya 2009). They are compatible with all types of insulating varnish, adhesive, transformer oil and other electrical equipment parts. Table 3 indicates that X-FIPER® meta-aramid paper X-630 has little change in dissipation factor under different type of chemicals. Table 4 exhibits that X-FIPER® X-630 meta-aramid paper has good resistance to oil type transformer oil and that the mechanical strength is retained even after 70 days exposure.

Table 3: Resist to acids and alkalis   (Meta-aramid Paper Testing Report, 2012)

Resist to acids and alkalis, compatible with all varnishes, resins oils, adhesives, fluorocarbons					
Meta-aramid paper thickness	0.05 mm	0.08 mm	0.13 mm	0.18 mm	0.25 mm
Contamination to transformer oil (change of dissipation factor %)	3×10^{-5}	3×10^{-5}	2×10^{-5}	1×10^{-5}	2×10^{-5}

Table 4: Compatibility testing with all varnishes, resins, oils, adhesives, fluorocarbons (Meta-aramid Paper Testing Report 2012)

Meta-aramid Paper				Thicknesses			
X630				0.05mm	0.08mm	0.13mm	0.18mm
Tensile strength N/cm	MD	Air		4.89	6.89	12.7	18.4
		Alcohol	70days	4.15	6.54	12.1	17.5
		Acetone		4.41	6.21	11.8	17.6
		Dimethylbenzene		4.76	6.97	12.2	17.6
		Silicon		4.88	6.87	12.3	17.3
		Transformer oil		4.64	6.74	12.8	17.8
	CD	Air		1.55	2.39	4.10	8.76
		Alcohol	70days	1.44	2.37	4.07	8.78
		Acetone		1.46	2.34	3.84	8.41
		Dimethylbenzene		1.57	2.42	4.18	8.03
		Silicon		1.52	2.38	3.92	8.55
		Transformer oil		1.55	2.50	4.30	8.60
Elongation %	MD	Air		6.64	6.58	6.06	9.61
		Alcohol	70days	8.03	10.4	9.89	12.5
		Acetone		10.1	9.72	10.7	13.4
		Dimethylbenzene		6.16	7.17	6.13	10.1
		Silicon		7.31	7.18	6.32	9.06
		Transformer oil		6.00	6.57	7.13	9.60
	CD	Air		4.43	4.31	4.87	6.72
		Alcohol	70days	4.84	5.52	7.53	10.7
		Acetone		6.17	6.55	6.92	10.3
		Dimethylbenzene		4.34	5.07	5.87	7.91
		Silicon		3.90	4.88	4.84	6.20
		Transformer oil		3.87	5.18	5.62	6.84

v. The Influence of Porosity

The rate or degree of resin, varnish, oil or adhesive penetration is important in electrical insulation for transformer and motor manufacturing because the electrical and mechanical properties are increased when insulation material is in transformer oil or impregnated with resin. There is a balance between good permeability and good varnish absorption, which ultimately relates to performance. Hence, a degree of porosity in the paper is required.

2.2.3   Summary and Next Steps

Potentially, the stated research objectives can be achieved by treating and coating a meta-aramid substrate with conductive polymers, as they would provide higher electrical conductivity, lighter-weight, and potential application as corona protection tape for wrapping conductor wire in high voltage motor and transformer industry.

Polymers are best known as insulating materials but polymers can also be chemically synthesized to exhibit characteristics as both a semi-conductive and conductive. The advantages of a conductive polymer are to have the conductive properties of metal with the ease of processing and properties of a polymer including flexibility and lighter-weight. In the previous chapter, the solution of combining insulator and conductor was proposed to take forward to product design. The purpose of the conductive layer is to provide a conductive structure which transfers the electrical potential from the conductor bar to the conductive tape layer, such that the conductor bar or wire, the conductive structure, and the conductive tape layer are all at the same electrical potential. The function of this new innovative product is to equalize the voltage over the length of insulated wire surface to guarantee a homogeneous distribution of electrical field in the ground insulation (Voith Hydro 2009). This product could be applied to an inner protection system for an electrical conductor bar/wire. As shown in Figure 12, the internal corona protection system acts to minimize internal coil partial discharge activity.
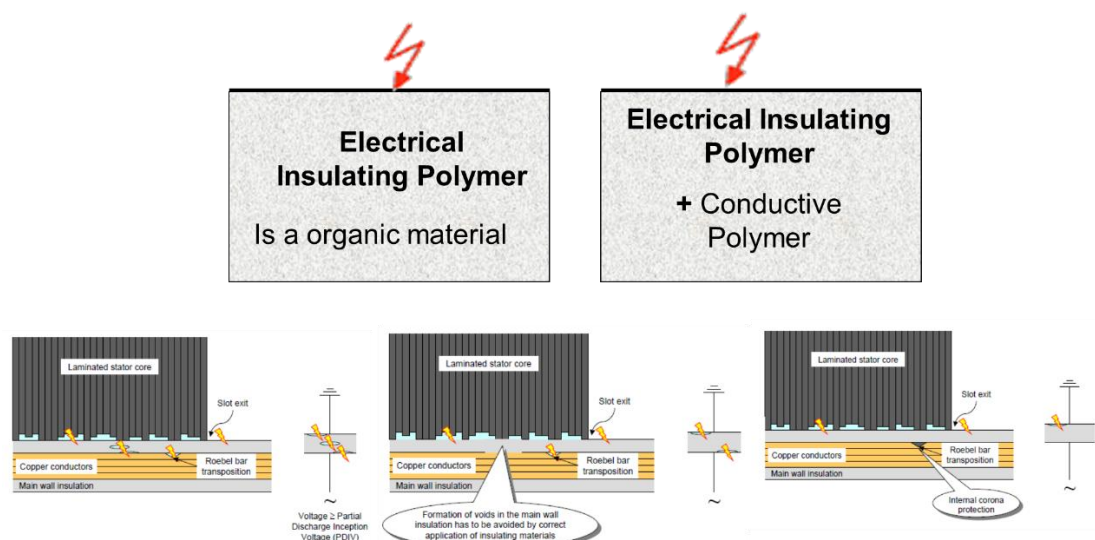
Figure 12: Product idea to solve partial discharge problem (drawing adapted from Von Roll training material 2012).

CHAPTER III - NEW PRODUCT DESIGN & SPECIFICATION

Previously, it was shown that meta-aramid, has competitive physical, thermal, mechanical properties and free volume or porosity that additionally allows good resin impregnation. However, because of the intrinsic insulating characteristics, specific strategies need to be developed to impart electrical activity to aramid paper. In this sense, the combination of aramid paper with ICPs allows to extend the functionality of aramid paper in corona protection in high voltage devices application. The objectives of this innovation product can be accomplished by treating and coating the meta-aramid substrates such as meta-aramid fibers, fibrids, base paper or calendering treated paper with conductive polymers.

3.1 Theoretical Property Requirement (Specification Development)

The innovative product requires an assessment of suitable properties including surface resistivity, tensile strength, and porosity in order to develop a specification.

3.1.1 Surface Resistivity Properties

A certain level of surface resistivity is required to avoid buildup of charge and provide an optimum electrical shielding in the particular application. Current commercialized product conductive meta-aramid paper by using carbon black has surface resistivity around 100 to 400 ohms/sq. (Fujiimori *et al.,* 2014), 100 to 400 ohms/sq. range of

surface resistivity is required to suit the application for the outside layers of the main wall insulation of coils in stators of high voltage motors. Furthermore, it is critical to have good control of the surface resistivity during the manufacturing process. With heat treatment above the glass transition, the surface resistivity is 4 to 5 times lower than the aramid conductive paper without heat treatment (Mikhail *et al.,* 2006). The glass transition temperature of meta-aramid is around 275° C. The surface resistivity can be measured by four-point probe resistivity meter. There is no standard testing specification for using a four-point probe resistivity meter.

3.1.2   Tensile Strength Properties

Tensile strength is another key characteristic. Conductive tape is wrapped around the conductor by an automatic machine and therefore, sufficient tensile strength is required to withstand breakage during the winding or meet the winding tension requirement. Tensile strength is dependent on the ratio of fiber and fibrid, the paper making process and the calendering process (Submission II Chapter 4). It can be measured by a Universal Testing Machine in tensile modes based upon the equivalent standards of China National Standard GB/T453-2002, International Standard ISO1924-2 and ASTM D828 (ASTM D828 2004). Commercially used DuPont[TM] Nomex® paper 410 at 0.05 mm thickness has a tensile strength of 39 N/cm for wrapping the conductive wire application. The objective here is to target a comparative figure of 39 N/cm, although it is common in industry practice to use 36N/cm as a requirement.

3.1.3   Impregnation Properties (Porosity)

To increase the mechanical strength and dielectric strength for applications such as high voltage motor, a resin impregnation will be utilized as standard industry practice. The paper structure must have sufficient porosity for resin impregnation. It is intended that

30

the conductive meta-aramid paper will retain porosity to allow resin to easily penetrate to fill the voids.   Porosity can be achieved by adjusting the ratio of fibers and fibrid and modifying the length and the diameter of the fiber.   Porosity can be measured by Air Permeance (Schopper Method) with the definition of ≤2 µm/Pa.s) based upon equivalent standards China National Standard QB/T1667, International Standard ISO5636/2 and TAPPI 5-460 (QB/T1667 2012).

3.1.4   Wire Wrapping Application - Thickness & Basic Weight

For application in dry type transformers, conductor insulation is normally required from 0.05 mm to 0.08 mm in thickness.   The thin tape for wire wrapping with the thickness of 0.05 mm is therefore most preferable to the transformer market maker.   For example, DuPont™ Nomex® 926 (conductor insulation tape) and 843 (conductive tape with carbon fiber for conductor wrapping) both have only 0.05 mm in the market place. In this project, the meta-aramid conductive is therefore targeted at 0.05 mm.   The paper thickness measurement can be measured based upon international standards ISO534：1995 or its equivalent China national GB/T451.3 and ASTM D374. (GB/T 451.3, 2002)

Density can affect performance in dielectric strength and tensile strength, higher density giving better performance.   The industry standard is measured with basic weight rather than the dimensions of density giving units of g/m^2 rather than g/m^3.   In the industry, the basic weight of the meta-aramid wire wrapping tape is from the range of 38-42 g/m^2.   Other meta-aramid paper manufacturers such as DuPont™ Nomex® 926 & 843 and Metastar's Y-15 are all around 40 g/m^2.   Therefore, this research project targeted the basic weight at 40 g/m^2 with tolerance +/-6 g/m^2. The basic weight can be measured by the international standard of ISO536 or its equivalent China national standard GB/T45.1-2002 or ASTM D646. (GB/T 451.2, 2002)

3.2 New Product: Definition of Property Specification and Advantages

Based on the previous discussion, a new product specification target is defined in Table 5.

Table 5: Target Parameter for product

Properties	Test Standard	Range	Unit	Target Value
Thickness	GB/T451.3-2002	0.048 – 0.065	mm	0.05
	ISO534			
	ASTM D374			
Basic Weight	GB/T45.1-2002	36-44	g/m²	40
	ISO536			
	ASTM D646			
Tensile strength	GB/T12914	Machine Direction	N/cm	39
	ISO1924-2			
	ASTM D828			
Air Permeance (Schopper Method)	GB/T1667		um/ (pa*sec)	≤ 2
	ISO5636/2			
	TAPPI T 460			
Surface Resistivity			ohms/sq.	100-400
Flame Retardant	UL 94			V-0
Rohs				Required
REACH				Required
Electrical Insulation System	UL 1446		°C	>/= 200
The target price is set less than the competitor at 30 to 50%				

Advantages of the new potential product over current existing products:

1. Higher thermal resistance (class 220°C) compared to mica type with polyester fleece type of conductive tape.

2. Free of binder resin (removal of the need to bond as no need to use binder resin) when compare with mica type of conductive tape.

3. No washing out of carbon/graphite particles during resin impregnation process.

4. High impregnability compared to DuPont™ product.

5. Can be taped with a taping machine and as well as this advantage, the new product can also use conventional taping equipment.

6. Enhanced conductivity compared current X-Fiper product.

3.3 Choice of Conductive Polymer

To select a candidate conductive polymer for this project, electrical, mechanical, thermal and chemical properties are to be considered.   Product accessibility (which is an important commercial consideration but unrelated to development), and ease of processing are the other main concerns.   The following is a summary of the outcomes of the findings of submission I with updates as required. A comparison of properties can be found in Table 6.

3.3.1   Polyacetylene

The first ICP to be discovered was polyacetylene, synthesized by Shirakawa Louis and his team (Shirakawa *et al.*, 1977).   It was discovered to have unique properties as the conductivity is similar to copper.   The developments of chemical reaction with the halogens using doping was extremely exciting to the world as the conductivity reached 10^5 Scm^{-1} while copper is 10^6 Scm^{-1}.   However, while the conductivity of polyacetylene is quite high, the environmental stability is poor.   Compared to other conductive materials such as polypyrrole (PPy) and PEDOT, the main drawback of polyacetylene is the processability and stability in the environment which makes it

currently unsuitable for this application. There is little current relevant research activity in this material.

3.3.2   *Polyaniline (PANi)*

Polyaniline (PANi) was known more than 150 years ago but was not developed as a potential commercial product until the last two decades. With its ease of synthesis and stability PANi has been developed in various applications, especially in the sectors of anti-static application as coating materials for corrosion resistance and in the aerospace industry.   PANi development is up to the stage that in its doped form it can be used as an extrinsically conductive polymer as blended with thermoplastic resins, with commercial application in EMI shielding, antistatic packaging, batteries etc.   (Aldissi 1992).   Current developments of waterborne polyaniline-graft-alkyd are successfully used for anticorrosion coating (Wang *et al.,* 2019).   PANi can also be coated on acetate film by using ionic layer adsorption which is of interest for waste reduction purposes and improved coating properties (Parel *et al.,* 2018).   The advantages of PANi is its diverse structural form, environmental stability and comparative low cost.   The major drawback is it is hard to process, non-biodegradable, rigid characteristic and has limited solubility.   Conductive polymer solubility and flexibility are needed for this project and thus, PANi is not the best choice here.

3.3.3   *Polypyrrole (PPy)*

PPy doped with aromatic sulfonates (mainly benzene or naphthalene sulfonates) have useful properties such as increased flexibility and a conductivity of 10^2 S cm^{-1} (Elschner *et al.,* 2011, pp.9-10).   PPy are already being commercialized for tantalum and aluminium capacitors in which PPy is used as a solid electrolyte coating (Cosnier *et al.,* 2010, p.215).   PPy has been attractive as a solid electrolyte because it has high

conductivity of the range from 10^1 to 10^2 S cm^{-1} and moderate environmental stability. In recent applications for example, Cellulose Nanofibre (CNF) were coated with PPy by chemical polymerization with iron chloride (III) as oxidant agent for the application of thin-film transistors or as biosensors (Lay *et al.*, 2016). The drawbacks however are toxicity and the high vapour pressure required for the monomer production because of the relatively high vapour pressure of the toxic pyrrole, Japanese workers had serious health risk by handling pyrrole in capacitor manufacturing) (Elschner *et al.*, 2010, pp.168). In addition, the intense colour and poor transparency are other disadvantages of this materials. Due to its molecular structure, a limitation of pure PPy is that once synthesised, it is hard to process it further as it is crystalline, and mechanically rigid (Kaur *et al.,* 2015). Thus, its rigidity, brittleness and insoluble nature rule it out as a suitable candidate for this project.

Table 6: Conductivity and other properties of common conjugated conducting polymers (Kaur *et al.,* 2015)

Polymer	Conductivity (S cm^{-1})	Type of doping	Properties	Limitations
Polyprrole	10-7.5 x 10^3	P	High electrical conductivity, ease of preparation and ease of surface modification	Rigid, brittle and insoluble
Polyanilline	30-200	n, P	Diverse structural forms, environmentally stable, low cost	Hard to process, non-biodegradable, limited solubility
Polythiophene	10-10^3	P	High electrical conductivity, ease of preparation, good optical property	Hard to process
PEDOT	0.4-400	n, P	Transparent conductor, environmentally and electrochemically stable	Limited solubility

3.3.4   PEDOT

Bayer AG, Leverkusen developed Poly(3-4-ethylene dioxythiophene), also known as PEDOT, in 1988, by combining oxygen-substituted polythiophenes and alkoxy-substituted thiophenes. PEDOT contains sulfur in the aromatic cycles.   With more than 20 years of evolution, PEDOT has become one of the best conducting polymers serving in technical applications in a range of different products today. Processing of PEDOT is much simpler than the processing of other conducting polymers and was found to be the most promising candidate material (Details in Submission I Section 3.4). Commercially it is often found as PEDOT:PSS where the PSS portion is actually an insulator material, but allows the PEDOT to be used in solution in combination. This will now be further explained, as well as the list of the key PEDOT:PSS advantageous properties over other CPs relevant to this project (Kaur *et al.,* 2015; Jagathessan *et al.*, 2014, p.333).

3.3.4.1   PEDOT: PSS

Figure 13 lists comparative advantages of PEDOT:PSS.

PEDOT:PSS advantages including transparency, low cost, low environmental impact, ease of deposition
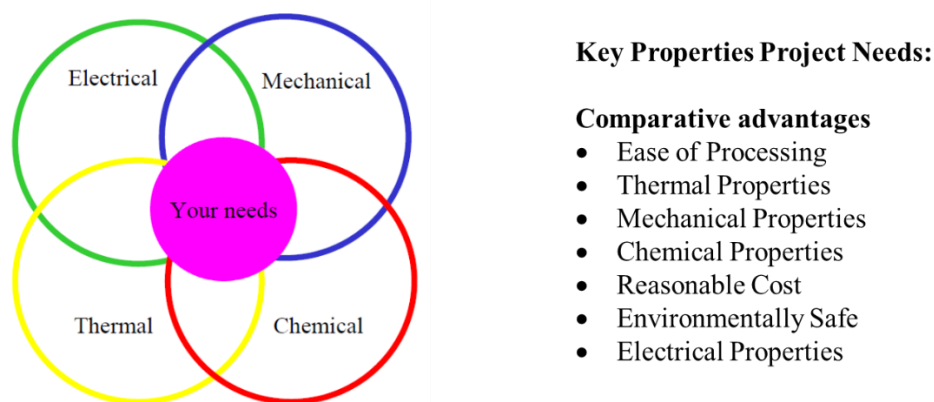
Figure 13: List of PEDOT:PSS comparative properties.

i)   Processing

One of the reasons why PEDOT:PSS was chosen in this project is the availability as a polymer dispersion.   By combining with poly(styrenesulfonic acid) (PSS) as a counter ion, a polyelectrolyte complex (PEC) can be produced that makes a stable dispersion, which can be reproduced on an industrial scale and can be used in many deposition techniques (Fundamentals of Conductive Polymer n.d.).   PEDOT:PSS dispersed in water can be deposited in principle by all common techniques including deposition of waterborne coatings (Elschner *et al.*, 2011, p.123), for example, inkjet and screen-printing, roll-printing, slot die and spin-coating or gravure printing and doctor blading. Production of conductive polymer PEDOT:PSS treated or coated on aramid (Lakshmanan *et al.*, 2008) and polyester fabric (Tadesse *et al*, 2017) have also been reported.

ii) Thermal Stability

Thermal stability is one of the advantages of using meta-aramid paper.   The conductive polymer being chosen here must also have the characteristic of thermal stability.   Thermal stability of PEDOT:PSS has been tested by thermogravimetric analysis (TGA) on thick layers. The weight loss and the ion currents of the relevant masses over time while the sample is heated at a constant rate in helium is less than 10%.   Based upon the analytical data obtained by TGA the material is considered to be thermally stable up to temperatures of 200 °C (Elschner *et al.*, 2011, p.124).   Recent research using TGA, has found decomposition temperature was almost the same before and after PEDOT:PSS coating.   Refer to the Chapter IV, Sections 4.5.7, 4.5.8 and 4.5.9 for more details. This was using a very thin layer or small quantity of PEDOT:PSS deposition of substrate fibers, including high performance fibers such as polyamide and aramid fibers.   In fact, PEDOT:PSS coated aramid fibers have better relative thermal stability as compared to the neat aramid fibers (Bashir *et al.,* 2017).

iii) Conductivity

The drawbacks of PEDOT-PSS are that it is infusible and insoluble (Cosnier *et al.,* 2010, p.215).   Also the surface resistivity requirement of the new product is 100 to 400 ohms/sq. whereon the maximum level of conductivity of PEDOT: PSS currently possible is up to 102 S cm^{-1}. The modification of the ratio of PEDOT to PSS will have direct impact on the conductivity as it determines the density of charge transporting PEDOT sites.   PEDOT:PSS exhibits a level of conductivity in the full range for conjugated polymers that has the conductivity ranked in the similar level toward metal materials such as silver and graphite. PEDOT:PSS can therefore achieve the goal in this project.   Furthermore, a recent research article from Bashir, *et al.,* (2017, pp.310-330) has made the conclusion that high performance textile fibers including polyamide

(PA6), aramid, aramid/PA6 hybrid and polyester fibers can successfully be functionalized by vapor phase polymerization (VPP) of PEDOT. The deposition of a dark-blue layer of PEDOT polymer on all substrate surfaces was the indication of successful coating and impregnation of PEDOT.

iv) Mechanical Properties - Flexibility

The conventional method for preparing electrically conductive tape for conductor wire is by mixing conductive solid fillers such as metal particles, carbon black, graphite or carbon nanotubes into the insulation type of polymers. The problem of, for example, carbon black is lack of flexibility and processability during the wire wrapping and resin impregnation processing. This creates the problem of the carbon black wear off from the backing and contaminates the insulation system within the electrical device such as high voltage transformer and motor. PEDOT:PSS is usually used in a thin film form deposited by spin coating. In the study of (Hokazono *et al*., 2014), they investigated the flexibility and thermal stability of films consisting of PEDOT:PSS, it was found that PEDOT:PSS films have both flexibility and mechanical toughness as well as relatively good thermal stability in air up to 3600 h. This is an indication of thermal stability of PEDOT:PSS. PEDOT:PSS is more flexible compared to coatings like carbon black and can be integrated into the material to consolidate the structure. PEDOT:PSS has stringed interdependence between chemical structural and electronic properties (Murugan *et al.,* 2005). Thus, it can be formed after coating and drying, this is very important for meta-aramid paper application in conductor wrapping process. In addition, a recent study has shown that by combining the mechanical properties of cellulose with the electrical properties of PEDOT:PSS a flexible paper can be produced as use as a material in electronic and electrochemical device; for example, supercapacitors (Wang *et al.*, 2018). Many attempts at making electrically conductive blends were performed in the resulting film, in the field of fiber spinning and cellulous

paper. The flexibility of PEDOT:PSS will resolve the issue from using metal or carbon particles in the conductive wrapping tape in conductor wire.

v)   Application and Opportunity

PEDOT:PSS is normally used on dispersions, pellets, and roll-to-roll processing on polymer substrates by slot die coating, inkjet or screen printing. Current commercialized applications are in Indium Tin Oxide (ITO) substitution coatings, membrane switches, capacitive sensors, displays and e-papers, organic light emitting diodes, antistatic coating and dispersion, photovoltaics, touchscreens, and super capacitors. There is no commercially available conductive polymer for an application on top of paper materials, therefore assessment on different forms of meta-aramid substrates need to be carried out and documented before selecting the appropriate method of depositing conductive polymer on the meta-aramid substrates. Recent research from (Bashir *et al.,* 2017) has indicated that high-performance fibers such as aramid (Twaron), polyamide (PA6), polyester (PET), and hybrid Twaron/PA6 fiber can be treated with conjugated polymer PEDOT:PSS to become electroactive fibers for use as smart materials for various medical, sports, and military applications. Most importantly, the mechanical properties such as tensile strength of these high performance fibers has not been affected after deposition with PEDOT. Current findings have shown some attempt at using PEDOT:PSS coated on the substrate of cellulose paper to produce electronic paper for electronic devices application. The paper roughness and porosity increase the contact area and enhance diffusion and capillarity (Morais *et al.*, 2018). In reference to the above example, meta-aramid has similar characteristics to cellulose paper in terms of porosity and roughness and therefore exhibits potential for success to integrate with PEDOT:PSS. In conclusion, this research has found that PEDOT:PSS is the most suitable target ICP for development.

CHAPTER IV - PRODUCT DEVELOPMENT

This section describes the experimental plan, processes, methods and results of integrating the meta-aramid materials with a conductive polymer solution of PEDOT:PSS.

A stage gate project management technique is utilised in which a new product development process is divided into distinct stages separated by decision points (Figure 14).   At each gate, continuation is decided by the project leader.   The decision is made on forecasts and information available at the time such as business case, risk analysis and availability of required resources.

4.1 Project Monitoring – Stage Gate
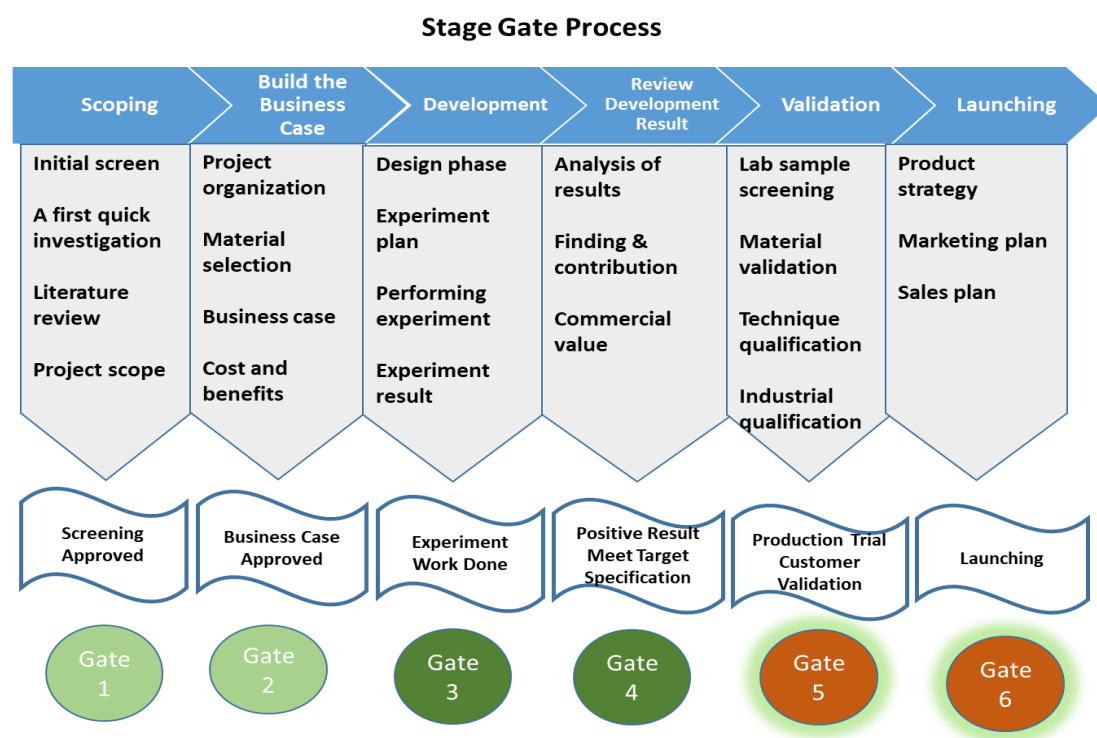
Figure 14: Stage-gate flow from initial screen to final launching.

This research involved major product innovation, the development process was designed in six stages. By using the stage gate process, unfeasible development was easily halted, significant costs and waste of raw materials can be reduced, and it allows increased communication among internal or external stakeholders. The project was designed in accordance with the project management systems described in X-Fiper Standard Operation Procedure (SOP) to have a formal project leader and project plan, which led to complete planning of tasks. Roles and responsibility of project stakeholder have been formally assigned (Table 7). The project leader is the decision maker at each stage. Each project member provides support per his or her function; for example, operation management, research and development, production implementation, process engineering, and testing and quality assurance. An advisory group at an executive level, and purchase level support is key to success for this research project in terms of financial and resources allocation to ensure adequate project resources in place. As the stage gate process is implemented in several stages, the decision points for whether or not to proceed to the next stage is outlined. In addition, gates are not just go or stop decision points, but also resource allocation and commitment points.

Table 7: Project team member and function

Team Leader	Department	Role in EngD Project	Stage Gate Function
Wai Kam Chung	General Manager Officer	Project leader: Leading the EngD Project & Stage Decision Maker	STAGE 1-6 Preparing, Implementation & Decision
	R& D Department	Product & process design, experiment, testing & result evaluation	STAGE 3, 4, 5
Supporting Team	**Department**	**Role in EngD Project**	**Stage Gate Function**
Production Manager – Polymer solution and Fiber	Production	Monitoring the polymerization and spinning production	STAGE 3
Production Manager – Fibrid and Paper	Production	Monitoring fibridation and paper making production	STAGE 3
Advisory Group	**Department**	**Role in EngD Project**	**Stage Gate Function**
General Manager/CTO	General Manager Office	Sponsor	STAGE 3
CFO	Financial	Reviewing the cost and benefit	STAGE 2
Purchase Supervisor	Purchase	Purchase materials needs for this project	STAGE 3
External Contact	**Department**	**Role in EngD Project**	**Function**
Key Account Sales Manager	Sales	Communicate customer needs	STAGE 1, 2 & 6
Von Roll, ABB, and Yau King., etc.	Technical & Procurement	Obtain product requirement and paper validation	STAGE 2, 5, & 6
Agfa Materials - Orgacon	R & D, Technical & Sales	Technical application support	STAGE 1 & 3

4.1.1   Project Planning

In Figure 14 stage gate 1, initial screening for the current product gap analysis, literature review and potential of the market has been studied.   The major drawback of the current product in the market has been identified; for example, the challenges of current product in application and the potential value for new innovative product is justified (Refer to the Section 1.3).   At stage gate 2, the manufacturing of this innovative product starts with a business plan including product definition and analysis and feasibility in which different departments assess the plan's chances of succeeding. The major function of planning is pulling resources together and accurately estimating the resource requirements, projecting how long key tasks will require, and preparing an effective "go forward" plan.   User needs and wants must be recognized (Section 2.2.2 and 3.1).   Since this innovative product was considered to have sufficient potential to generate turnover, the project leader decision is to go and the stage gate 2 is open to go to the stage 3 (Development).

Stage gate 4 was the evaluation of the experiment testing result and the feasibility to forecast to the final stage.   Stage gate 5 is production trial, customer validation and industry certification availability such as UL 94, UL 1446, RoHS and REACH (Table 5).   The final stage is product launching via marketing planning including sales force, training, preparation of marketing collaterals, ordering raw materials, etc. (Refer to the Submission IV).   This final gate will be opened once customer verification, field evaluation and the future work are done.

4.1.2 Business Case

It is necessary to convince the sponsor company to realize the potential value of this new product in order to allow this project to continue. Therefore, some background to the company and market is provided here. X-Fiper, is a family owned company with a total of approximately 380 employees, is a recognized market leader in the fields of insulation products and systems for the electrical machinery industry, as well as for lamination materials and parts for various applications. X-Fiper also provides special thermal and fire resistant insulation products of meta-aramid fiber and paper to both the electronics and other industries. To expand the product range and presence in the market place, the business project leader is requested to identify the business opportunities for the product "innovative conductive meta-aramid paper" to assess whether it can be translated into a potentially valuable investment proposal. The new product of conductive meta-aramid tape would add value to the current X-Fiper product range apply into the same market segments. X-Fiper has product X630 or X630-H meta-aramid insulation paper for the market of insulation conductor wrapping application in high voltage rotating equipment and high voltage transformers. By adding conductive polymer to enhance the conductivity property of the current product it may be suitable for the application for corona protection. The total market size including the segment growth of high voltage transformer, rotating machine and the competition have been elaborated in Submission IV Chapter 3.

A cost benefit analysis is used to evaluate the total anticipated cost of a project compared to the total expected benefits in order to determine whether the proposed implementation is worthwhile for a company or project team. The following is the projected sales and cost based upon the current customers such as ABB, Siemens, and some local customers with projected total sales from year of 2021 to 2025. The capital investment might involve coating equipment that assumes RMB 100,000 to 200,000

(US$ 15,000 to 30,000) depending on the sophistication of the equipment selected for manufacturing. The five year sales projection from this new product reflects an additional 15% sales volume growth in dollar amount by year 5.   Based upon the analysis of the potential sales for five years and the manufacturing cost including the materials costs, the projected benefits from sales are greater than the total production costs.   Thus, X-Fiper management decided that the proposed conductive meta-aramid paper is potentially a worthwhile project to move forward to the development stage. Table 8 is the summary of 5 years projection sales vs. cost (only considering the manufacturing cost and raw material cost) for reference.

Design Failure Mode Effects Analysis (DFMEA) was evaluated and completed to identify relative risks. Major risks are addressed and planned, adding steps that ensured success.   For example, to avoid contamination, additional cleaning procedures were added to the experiments. All the lab instruments or production equipment involved in this project required detailed cleaning immediately after the conductive meta-aramid experiment were done.   Normal meta-aramid paper products were made right after the conductive meta-aramid paper experiments were tested to ensure obtained normal insulation properties.

Table 8: Cost and benefit analysis based upon 5 year potential sales and basic manufacturing and raw material cost

	Total Sales : 1,000 RMB			2021	2022	2023	2024	2025
	Developed Products	000' RMB*	0	4,000	12,000	24,000	40,000	60,000
		Tons*		10	30	60	100	150
	Raw Materials (RM) Cost			1,300	3,900	7,800	13,000	19,500
Manufacturing and RM cost	Manufacturer (Manu.) Cost		24.6% of total Sales	984	2,952	5,904	9,840	14,760
	Total of RM and Manu. Cost			2,284	6,852	13,704	22,840	34,260

Based on this projection and discussions with the advisory group, approval was granted to continue as evidenced in the opening stage gate 3 and evidence for 5 and 6, whilst

also satisfying the partial requirement of stage gate 5 (experimental results are the other requirement).

4.1.3 Intellectual Property Management

X-Fiper has actively engaged in meta-aramid technology research and development, achieving solid growth as an R & D driven company in creating markets and customer segments by developing products with proprietary technologies. Intellectual property (IP) activities in X-Fiper are vital to support sustainable business operations. The outcome of R & D activities are products and IP. Therefore, X-Fiper takes a strict, consistent approach against counterfeit materials and intellectual property held by others without permission. It manages the intellectual property rights from the standpoint of optimizing the overall intellectual property portfolio including trade name, trade mark and patent. Currently, X-Fiper has a much stronger position in the China domestic market than globally. X-Fiper wishes to expand the global customer thus strengthening the differentiation versus its main competitors. Therefore, at the initial stage, a patent was applied in the local base, then spread to the global basis. For this new product of conductive meta-aramid paper, X-Fiper applied for the China patent via the application number of CN201510153566.2A in year of 2015. The application was granted on June 23, 2017 with the patent number of CN104818654B "Production Process of Conductive Meta-aramid Paper and Tape" by the author of H. Zhong and S.M. Ho. It is company practice that the owners name goes on the patent.

4.2 The Development Stage

The development stage (Stage Gate 3) includes the design phase. The prototype conductive polymer meta-aramid conductive paper was prepared in the X-FIPER research and development laboratory. With the process to manufacture the

47

electrically conductive polymer in place, the concept of utilizing CPs has been moved from a theory to a reality. The global electrical industry has been waiting for someone to develop the process and provide the technical acceptance of the concept. The experimental plan is based on the base chemistry of meta-aramid as the central part of the larger molecular structure; the same meta-aramid component which is well established and accepted by the industry and enhancing electrical properties by integrating conductive polymer.

Two key experiments were planned:

1. Complete the molecular structure using primarily the meta-aramid linkage
2. Complete the molecular structure by adding an electrically conductive component PEDOT:PSS into the total structure

4.2.1 What is to be achieved

For the purpose of getting sufficient data, laboratory scale experimental work was needed. The form, process and the ratio of PEDOT:PSS for the future production runs must be examined and refined through experiments and analysis. The form and process has been identified based upon the experiments. Electrical properties have been measured. Once the form and process were determined, the optimum ratio of PEDOT:PSS could be identified. To satisfy stage 4 and provide evidence for stage 5 rigorous validation of the hypothesis is needed to test.

Additional needs for major equipment for future production are not within the scope of this thesis. Major changes to the PEDOT:PSS conductive polymer and the options for the use of other conductive polymer are also beyond the scope of these experiments.

4.3 Experimental Design

Conducting polymers must have the mechanical properties, electrical conductivity, process ability as well as being compatible with other materials. This has been the major challenge in application of this class of polymers for electrical insulation system in high voltage applications. Development of new material/composites of conducting polymers along with non-conducting polymers to retain mechanical performance, and thermal characteristic, while enhancing the conductivity or surface resistivity meets the performance requirements of the industry. Theoretically, the process could be in the form of a blend or composite or coating in order to combine the useful properties of both materials. The major challenges thus lie in selection of conductive polymer, achieving a low percolation threshold and retaining conductivity.

4.3.1   Possible Ways of Integrating Meta-aramid and PEDOT:PSS

For commercial and cost purposes, the ultimate goal is to achieve reasonable electrical conductivity with the lowest possible amount of conductive polymer, while retaining the properties of meta-aramid polymer. Paper can be made by combining the conductive polymer aramid pulp with other, usual, components of an aramid paper on a paper making machine. It can also, be made by combining all of the components of an aramid paper and adding the conductive polymer, for example as an aqueous solution, at the paper making machine. The following list contains the process innovations targeted by the author in the research experiments. The experiments evaluated the possible ways of integrating meta-aramid and PEDOT:PSS as well as seeking the appropriate methodology for making the meta-aramid conductive tape for corona protection.

The following are the options evaluated:

i)   The meta-aramid polymer solution is the original raw materials to form the short cut fibers and fibrids, the conductive polymer is applied during the synthesis process.

ii) Conductive polymer is polymerized or coated over the meta-aramid short cut fibers or fibrids.

iii) Conductive polymer is coated – the process is to immerse the base paper into the conductive polymer fluid and then pass the coated paper through a calendering machine to obtain the meta-aramid composite paper.

iv) Meta-aramid polymer chemistry modified to incorporate the conductive component into the molecular structure.

4.3.2   *Conductive Material to be Produced*

The program has involved integrating one new material and developing a new process within the current production process. The following are the materials needed:

i)   Meta-aramid

Meta-aramid has distinct synthetic fiber manufacturing technology and because of the long-chain polymer molecules it possesses enhanced heat resistance and tensile strength properties. The two molecular chains are arranged so as to form a zigzag aramid fiber, it is also called meta-aramid (Figure 15). It is investigated in five forms which is designed P1, S1, F1, B1 and C1 within this work (Table 9). Details of each meta-aramid specimen production process is exhibited in Submission II Chapter 5. The following is the summary.
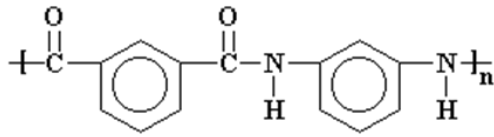
In Nomex the aromatic groups are all linked into the backbone chain through the 1 and 3 positions. This is called *meta-* linkage.

Figure 15: Electrical insulation material - Nomex® Meta-aramid (n.d.).

Table 9: Experiment material and process to be involved

	Process	Outcome Specimens			
		Normal Specimen	PEDOT:PSS Specimen		
Polymerization Process - Polymer Solution	P1: Normal production polymerization process; P2: Add PEDOT:PSS solution to the P1 solution	P1	P2		
Polymerization Process - Polymer Solution	S1: Normal Spinning production Process by using P1 polymer solution; S2: coating S1 with PEDOT:PSS in the Lab (for further test purpose)	S1	S2		
Fibridation - Fibrid	F1: Normal Fibridation production Process by using P1 polymer solution; F2: forming fibrid film from P2 with PEDOT:PSS in lab (for observation)	F1	F2		
Paper Making - Base Paper	B1:Normal Paper Making production process by mixing S1 and F1 via paper machine; B2: coating B1 base paper with PEDOT:PSS in the lab; B3: Specimens of S2 mix with F1 forming B3 via the paper making machine	B1	S1+F1 = B2	S2+F1 = B3	
Calendering - Final Paper	C1: Normal calendering process; C2: Calendering process on B2; C3: Calendering Process on B3; C4: Coated PEDOT:PSS on C1	C1	C2	C3	C4

1. Meta-aramid Solution – P1 & P2

Meta-aramid polymer solution (P1) is the major ingredient of making meta-aramid fiber and fibrid. The meta-aramid polymer was produced using m-phenylendiamine and dichloride of m-isopthalic acid. The in-house polymerization process of meta-aramid monomer is to use a defined solvent for example Dimethylacetamide (DMAc) or N-methyl pyrrolidone (NMP) and synthesis in solution state (Figure 16). The meta-aramid solution is formed and then put into storage conditions and protected away from contact with oxygen (Figure 16). The intermediate product of meta-aramid solution is controlled and measured by solid content and viscosity. After polymerization, the meta-aramid polymer solution can be processed in two different processes to produce meta-aramid fiber and meta-aramid fibrid. There is a process control difference to produce either fiber and fibrid; thus, this is confidential to the company.

Conductive meta-aramid polymer solution (P2) is formed by adding aqueous version PEDOT:PSS polymer in the laboratory. This sample was based on the optimal formulation as of 1% wt. which reached the project requirement for surface resistivity.

2. Meta-aramid Fibers – S1 & S2

Meta-aramid fibers (S1) can be produced by either wet-or dry spinning processes, wet spinning is used to produce nearly all commercial precursor fibers. For wet-spinning processes, the meta-aramid solution (from polymerization) is first dissolved in a solvent. The meta-aramid solution is then extruded through a thin plate containing thousands of capillaries to form meta-aramid fiber. (Figure 16)

Conductive meta-aramid polymer fiber (S2) sample is formed from coating the surface of S1 with PEDOT:PSS solution in the laboratory. This sample was run at the optimal percentage which was found to be 1% wt.

Meta-aramid Polymer Solution (P1) and Fiber (S1)

Polymerization and fiber making process
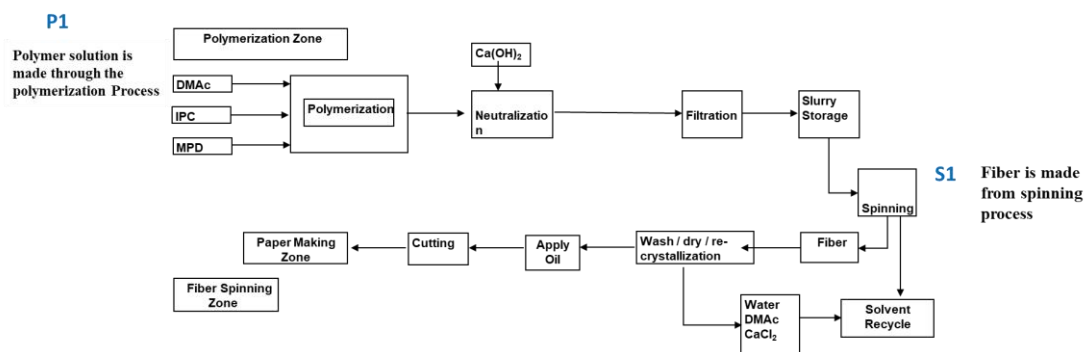
The aramid fiber of this invention is made from aromatic polyamide fiber, wherein at least 85% of the amide (--CONH--) linkages are attached directly to two aromatic rings.

Figure 16: In-house production process of meta-aramid polymer solution and fiber.

3. Meta-aramid Fibrid - F1 & F2

Meta-aramid fibrid (F1) is made from the meta-aramid polymer solution, mixed with solvent in the formulated ratio and concentration. It then goes through the fibridation equipment to obtain the required structure or surface dimension. The doped meta-aramid fibrid is then washed with deionized water to eliminate the solvent. Meta-aramid fibrid is ready to be used. (Figure 17)

Conductive meta-aramid fibrid (F2) film sample was formed from using P2 with PEDOT:PSS in the laboratory.

4. Meta-aramid Base Paper - B1, B2 & B3

Ratio of fiber and fibrid is formulated as required and then mixed together with deionized water. The mixed slurry is pumped into the Fourdrinier paper machine and wet-laid in a net to a form wet-paper. To remove excess water, a vacuum pressure de-watering process in the paper making machine is executed. The wet-paper of meta-aramid base paper (B1) then goes through drying process to complete the evaporation of any remaining excess water. (Figure 17 & 18)

53

Conductive meta-aramid base paper (B2) sample is formed by impregnated B1 with PEDOT:PSS in the laboratory.   This was run at varies percentages from 0.01% to 1%

Conductive meta-aramid base paper (B3) sample is established by S2 obtained from experiment and F1 to made an handsheet paper by Rapid Kothen Sheet Former in the laboratory.

5.   Final Calendering Meta-aramid Paper – C1, C2, C3, & C4

For final calendering Meta-aramid paper (C1), the calendaring process is performed to improve the mechanical strength such as the tensile strength by increasing the density. Figure 17 illustrates the process and Figure 18 demonstrates the structure change from base paper to calender paper.   The density cannot be more than 1 g/cm³ because then pores in the paper decrease which finally affects the porosity function. The calendaring process cultivates the compression and increases the density to a certain specific level to reach required properties (Submission II Section 4.2.1 c)

Conductive meta-aramid calendering paper (C2) is made by calendering the sample B2 obtained from experiment.

Conductive meta-aramid calendering paper (C3) is formed by calendering the sample of B3 obtained from experiment.

Conductive meta-aramid calendering paper (C4) is formed by brushing PEDOT:PSS ink on the C1.

Meta-aramid fibrid (F1), Base Paper (B1), & Calendering Paper (C1)

Base and calendering making process

F1 Prepare the Fibrid: Aramid fibrids used as binder materials and can be prepared using fibridating for the purpose of this invention

B1 Based paper is formed from Paper making machine
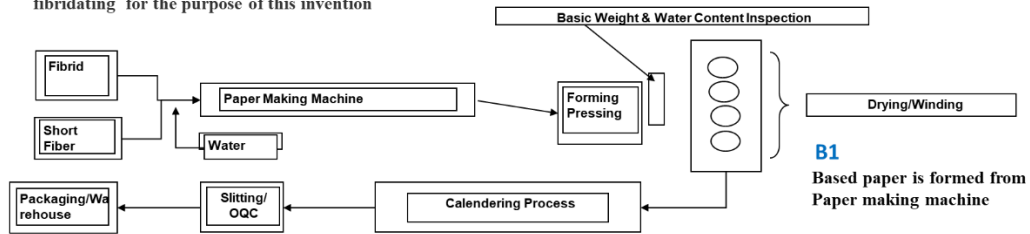
C1 To improve the mechanical properties and smoothness, hot press with pressure calendering process is used.

Figure 17: Base and calendering paper making processes.
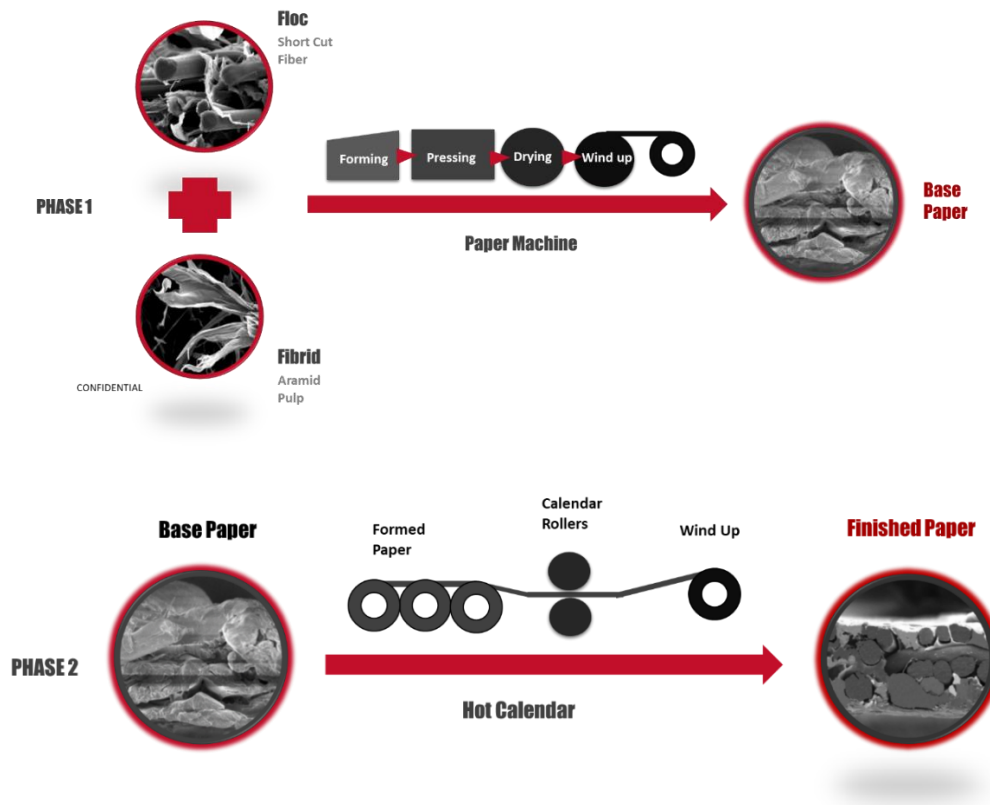
Figure 18: The process of paper making and calendering, and the structure changes from meta-aramid base paper to calendering paper.

ii)   PEDOT:PSS – "2"

PEDOT:PSS an inorganic conductive based-material which shows a combination of high transparency, is conductive, high flexibility and high processability.   During integrating of PEDOT:PSS with meta-aramid specimens for example under a coating processes, coated deposition and solvent evaporation are carefully observed. Aqueous version of PEDOT:PSS has been used for all the paper making experiments. Ink version has been used for comparative purpose.

The PEDOT:PSS material is supplied by Agfa Materials group with product named Orgacon®. Originally, an Orgacon® PEDOT:PSS ink version of conductive polymer was chosen (Orgacon n.d.）; after performing different dilution of experiments, it was discovered that the current application is not sufficient.   The coatings were not able to be produced uniformly. After several discussions with Agfa's engineers, the cooperation between the two parties started and they helped design and deliver the research plan.   By working directly with our lab engineer and research team, the Agfa researcher was able to customize a technological development of a solution-based high throughput manufacturing process for a modified aqueous version for the purpose of antistatic coating and dispersion.   For integrating PEDOT:PSS to fibridation, spinning, paper making, and calendaring process, PEDOT:PSS was customized to a new version with a specification as ready to use formulation.   The other major reason aqueous version is better than ink version in this research experiment is that it contains over 98% water instead of additive and resin in the ink version.   Other additives or resins contained in the ink version, might affect the meta-aramid thermal resistance.   As a comparison purpose, the ink version can be evaluated by coating method to make up a prototype after the calendaring process is applied (C4) (Table 10).

Table 10: PEDOT:PSS aqueous and ink version specification

ORGACON™ PEDOT:PSS			
	Unit	Aqueous	Printing Ink
Part No		ICP1050S	EL-P5015S
Active Chemical	% wt.	1.1-1.3	0.8
Colour		Blue	Dark Blue
pH		1.5 - 2.5	2.5 - 5.5
Viscosity	mPas	35	100
Thermal Cure	°C/minute	130/6	130/6
Surface Resistivity	ohms/sq.	120	125

4.4 Test Method, Sample Preparing and Measurement Strategy

4.4.1 Test Methods

i) Single Fiber Tensile Strength Test

An ASTM D322 testing method was used with a single fiber strength tester to test the tension strength and elongation of the meta-aramid fiber. This test method covers the measurement of tensile properties of meta-aramid single fiber of sufficient length to permit mounting test specimens in a tensile testing machine. Equipment was calibrated before use and the testing lab environment retained 23 °C ± 0.6 °C and 45 % RH ± 5 %RH. The single fiber specimens are tested at a constant rate of extension. Using the force elongation curve, the breaking force and elongation at break are determined (Single Fiber Tensile Strength measurement at the unit of cN/dtex). Ten specimens are tested and average recorded. The test was done by X-Fiper testing laboratory.

ii) Surface Resistivity

The four-point probe method is the most common way to measure a semiconductor material's resistivity (Friedberg 2002).   This technique can measure either bulk or thin film specimens.   The tester contains four thin collinear tungsten wires which are made to contact the sample under test.   Two of the probes are used to source current and the other two probes are used to measure voltage.   The surface resistivity meter has two measurement ranges from 0.00 to 2,000 and 0.00 to 20,000 with an accuracy of 1.4 ohms/sq. @ 1000 ohms/sq.   Equipment was calibrated before used and the testing lab environment retained 23 °C ± 0.6 °C and 45 %RH ± 5 %RH.   Five specimens were prepared and 5 measures per each specimens were recorded for a total of 25 measurements per paper construction.   The average measure was calculated and used for comparison analysis.   The surface resistivity is using the unit of ohms/sq. The test was done by X-Fiper testing laboratory.

iii) Basic Weight

This test method covers the determination of the mass per unit area of meta-aramid paper.   In the SI metric unit system, the mass per unit area of paper is expressed in grams per square meter (g/m^2).   For the meta-aramid paper, we take the total weight of one piece of paper cut to the basis size.   This gives us our basis weight.   Figure 19 exhibits the procedures of measuring basic weight based upon testing standard GB/T451.2-2002 (ISO534) or equivalent standard ASTM D 646. （GB/T451.2 2002） The standard testing environment requests room temperature of 23°C +/-2°C and relative humidity at 50% +/-5%.   Equipment was calibrated before used and the test was done by X-Fiper testing laboratory.

58
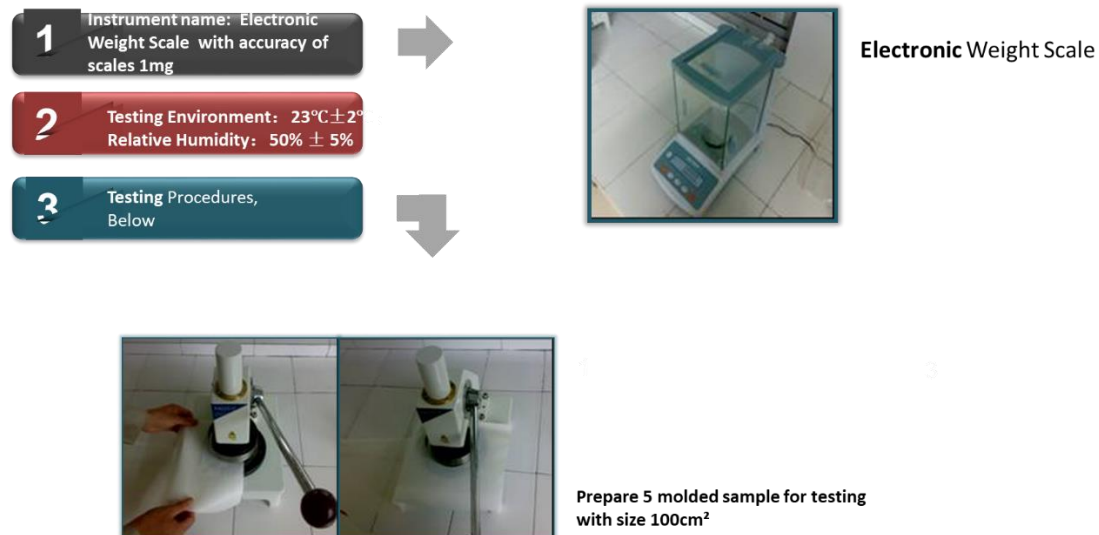
Figure 19: Measuring the basic weight based upon testing standard GB/T45.1-2002 (ISO534).

iv) Air Permeability Test

For the measurement of the porosity, an air permeability test is performed. The testing method is able to determine the air permeance of papers and boards which have air permeances between 0.1 μm/(Pa*sec) and 100 μm/(Pa*sec). According to the testing standard T460 (Walkinshaw 2006), this method measures the amount of time required for a certain volume of air to pass through a test specimen. The air pressure is generated by a gravity-loaded cylinder that captures an air volume within a chamber using a liquid seal. This pressurized volume of air is directed to the clamping gasket ring, which holds the test specimen. Air that passes through the paper specimen escapes to atmosphere through holes in the downstream clamping plate. The testing standard is based upon GB/T1667 (ISO5636/2) or equivalent TAPPI T-460. （QB/T1667 1998） Figure 20 shows the steps and calculation of air permeability of specimen. The standard testing environment requests room temperature of 23°C +/- 2°C and relative humidity at 50% +/-5%. Equipment was calibrated before used and the test was done by X-Fiper testing laboratory.
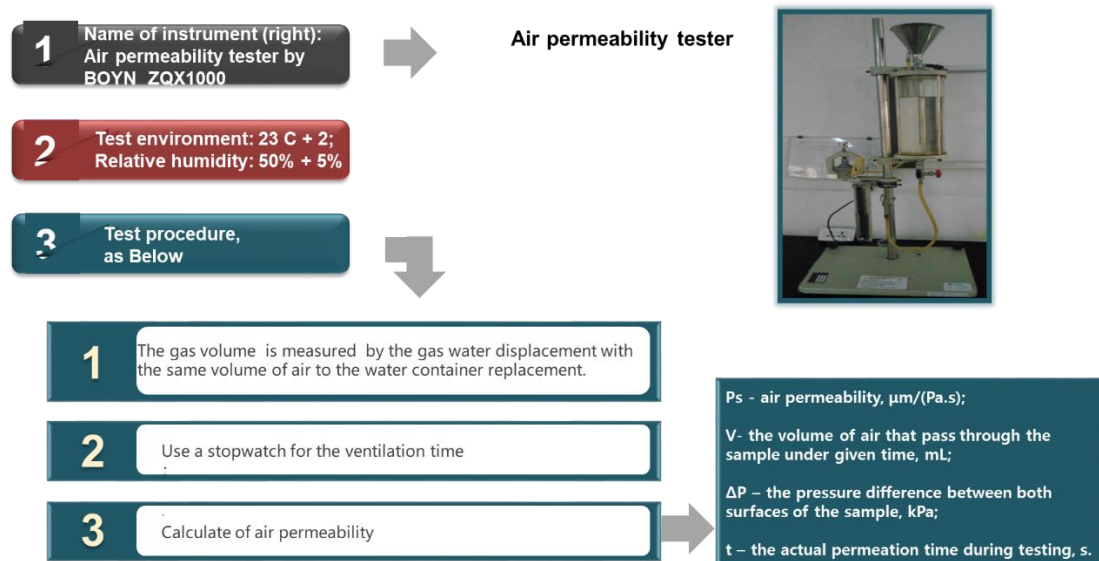
Figure 20: X-Fiper procedure for measuring air permeability based upon the testing standard GB/T1667 (ISO5636/2).

v) Tensile Strength

Tensile Strength refers to the capacity of a material to withstand loads while being stretched or pulled before breaking. It is normally measured by a Universal Testing Machine in tensile mode (Introduction to Tensile Strength 2004). In paper manufacturing it is known that orientation of the fibers is a key factor in mechanical properties, and tensile strength is the most important measure for those properties. The direction with higher alignment has improved tensile properties. Within the preform structures there are two major in-plane directions of alignment, the machine-direction and the cross machine-direction. The tensile properties of both are taken into consideration during testing (ASTM International 2004).   The testing standard is based upon GB/T12914 (ISO 1924-2) or equivalent standard ASTM D828. The standard testing environment requests room temperature of 23°C +/-2°C and relative humidity at 50% +/-5%.   Equipment was calibrated before use and the test is done by X-Fiper testing lab. In the case of paper or other thin webs, tensile strength is then defined as the breaking force (load) per standard width of the specimen; for example,

in the present experiment, the tensile strength of paper is determined in units of kN/m or N/cm (i.e maximum force per unit width).   In this paper, N/cm has to be used. Figure 21 exhibits the sample preparing in terms of procedures and size, the procedures of testing, and the testing result.
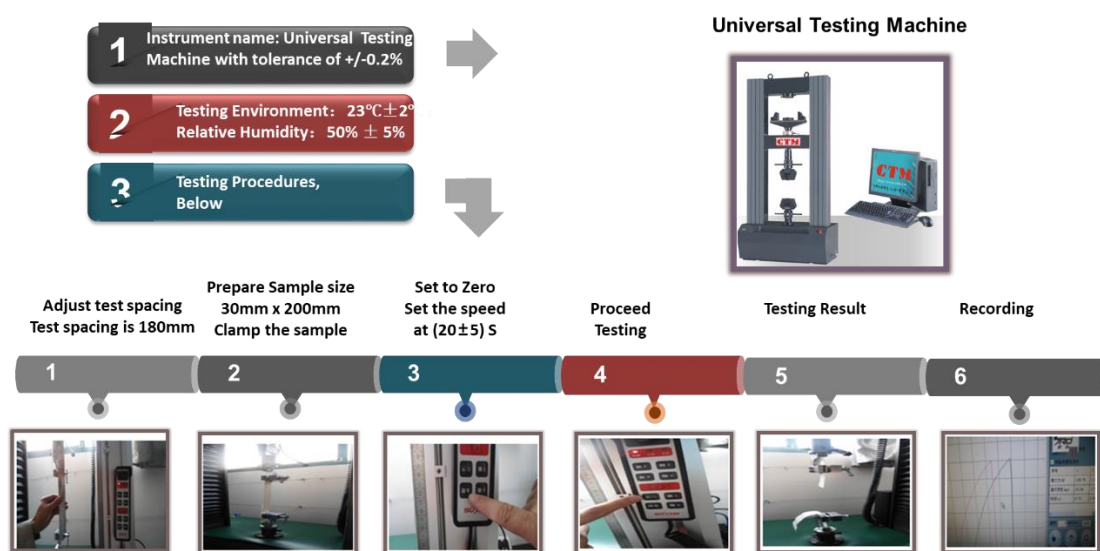
Figure 21: X-Fiper procedures for measuring the tensile strength based upon the testing standard GB/T12914 (ISO192402).

vi) Differential Scanning Calorimeter (DSC)

Using DSC, glass transition temperature, melting point, and the amount of energy which a sample absorbs while melting, crystallization point and the amount of energy a specimen releases while crystallizing can be measured.   The specimen weight of 10 to 15 mg is heated at a controlled rate as specified in the standard and a plot of heat flow versus temperature is produced.   The resulting thermal scan is then analysed. The DSC test method is based upon the reference standard JY/T014-1996 and testing method N2, a scan was done between 25-300°C at 20°C/minute.   The test was done by Weipu Jishu Testing Laboratory on behalf of X-Fiper.

vii) Fourier-Transform Infrared Spectroscopy (FTIR) for Material Identification

The FTIR Spectrometer generates a graph in the form of an absorbance spectra, which shows the unique chemical bonds and the molecular structure of the specimen material (Intertek, 2019).   During testing, when infrared radiation is passed through a specimen, some radiation is absorbed by the specimen and the rest passes through.   This absorption spectrum will have peaks representing functional groups (e.g. meta-aramid, chlorides, etc.) different types of bonds, and thus different functional groups, absorb infrared radiation of different wavelengths.   Qualitative information about the specimen is provided.   The FTIR test method was based upon the reference standard JY/T 001-1996 and was done by Weipu Jishu Testing Laboratory on behalf of X-Fiper.

viii) Thermogravimetric Analysis (TGA)

TGA is an essential laboratory tool used for material characterization.   By heating a material any weight increase or decrease can be identified.   By reviewing the weight changes, it can be understood at what temperature the weight loss begins.   The simple size should be between 2 and 50mg.   The material decomposes in two steps, first rapidly, then slows as the last remaining material decomposes. When comparing samples with two identical testing method conditions, the differences are easily displayed (Perkin 2018).   The TGA test method is based upon the reference standard JY/T014-1996 and testing method N2, a scan was done between 25-400°C at 10°C/minute.   The test is done by Weipu Jishu Testing Laboratory on behalf of X-Fiper.

4.4.2 Measurement Strategy

For prototype testing, it is necessary to verify and validate the product performance. It is not always possible to control all of the conditions of a test, but a multitude of repeat tests can narrow the chance of error. Therefore, each experiment needs to be done more than once due to the potential for unforeseen variation. In this project, each experiment is planned for repeat at least five times/trials based upon industrial standard.

4.5 Experiments

4.5.1 Preparation and Characterisation of PEDOT:PSS Coated Fibers (S2)

The purpose of this experiment is to make specimens of S2 (Figure 22)

1. Material List

   a) S1

      i. Length of fiber at 300 mm

      ii. Density at 1.8 dtex

      iii. Tensile strength at 4.8 cN/dtex

   b) Orgacon® PEDOT:PSS as supplied

   c) Deionized water (pH: 5.0 -9.0 and conductivity: ≤ 50 based upon X-Fiper testing procedures)

2. Test Specimen Preparation

   a) S1

      i. Prepare a total of 720 fiber pieces, each 300 mm in length of S1, placed all the test specimens into an oven at 100 °C for 60 minutes to eliminate the

moisture. Test groups of 5 test specimens.   Each test described below was performed using a new test set of 5 test specimens.

    ii.   Measure the surface resistance

   iii.   Measure the tensile strength

  b) PEDOT:PSS

Prepare 500 ml glass container with 200 ml solution of PEDOT:PSS

3. Equipment

  a)   Vacuum oven

  b)   Pipette

4. Experimental Process

  a) Impregnated new test sets of the S1 group for 1 minutes to form test material S2 (fibers immersed in PEDOT:PSS solution)

  b) S2 test specimens were then placed into the oven at a temperature of 100°C for 10 minutes' heat treatment

  c) S2 tested and recorded tensile strength and surface resistance

  d) S2 is rinse water, dried and retested

S1 & S2

Meta-aramid
Fiber
S1

(S1 is made from
Normal meta-aramid
Spinning Process)

Conductive Meta-
aramid Fiber
S2

(Impregnated Meta-
aramid Fiber S1 in the
PEDOT:PSS solution)

Remark: S2: By adding PEDOT:PSS by impregnation process – color changed from creamy white to light blue
After the Water Rinse process, the colour changed from light blue to lighter blue

Figure 22: Transforming S1 to S2.

5. Results

a) Surface resistivity result

S2 results (25 points from 5 specimens).   Table 11 summarizes the measurements. From Table 11, it can be seen S2 has an average surface resistance at 106 ohms/sq. From this result, it can be concluded that PEDOT:PSS enhances the conductivity when incorporated at 1% in S1.   (For S1, the surface resistance was over the measurement limit)

b) Water rinse result

To imitate the normal meta-aramid paper making process, meta-aramid fiber needed to have a water washing process.   The measurement of 5 specimens with 25 data points exhibit a value over the measurement limit of 20,000 ohms/sq. from the surface resistivity meter.   Based upon this experiment, the meta-aramid fiber failed to provide adequate adhesion for PEDOT/PSS.   It is concluded that PEDOT:PSS could not be integrated with meta-aramid fiber by using dipping method.

c) Tensile strength result

The tensile strength evaluation of S2 showed no measurable impact after the PEDOT:PSS adhered to the s (Table 12).

Table 11: Surface resistivity measures of conductive meta-aramid fiber S2

5 Sets of Samples	S2 Surface Resistivity Measurements Ohms/sq.					
	1	2	3	4	5	Average Value
(a)	65	100	120	110	100	99
(b)	70	150	100	80	120	104
(c)	120	85	100	120	130	111
(d)	100	110	130	100	130	114
(e)	120	100	70	100	120	102
S2: Mean						106
Coefficient Std. Deviation						5.3

Table 12: Comparison of S1 and S2 in single fiber tensile strength

Single Fiber Tensile Strength (Average Value) cN/dtex		
5 set of Samples	S1	S2
(a)	4.50	4.50
(b)	4.38	4.40
(c)	4.40	4.40
(d)	4.36	4.30
(e)	4.38	4.36
Mean	4.40	4.39

4.5.2 *Preparation and Characterisation of Polymer P2 and fibrid F2 (with PEDOT:PSS)*

The purpose of this experiment is to see it is feasible to add PEDOT:PSS into meta-aramid polymer solution P1 to form conductive meta-aramid polymer solution P2. The second purpose is to review how F2 is formed from P2, and what is the impact on surface resistivity. The third purpose is then to review the thermal behaviour of conductive meta-aramid fibrid sheet F2. The lab sample of F1 is made out of P1 being defined as the control sample to compare with F2.

1. Material List
   a) P1
   a) F1
   b) F2
   c) PEDOT:PSS as supplied
   d) Deionized water (pH: 5.0 -9.0 and conductivity: ≤ 50 based upon X-Fiper testing procedures)

2. Equipment
   a) 2 of 300 ml glass bottle of container
   b) 2 pieces of glass plate at the size of 100 cm x 100 cm
   c) Ultrasonic equipment (SK5210HP from Kudos)
   d) Glass stirrer
   e) Pipette
   f) Vacuum oven

3. Test Specimen Preparation

    a) Prepare 2 300 ml bottle of 50 ml P1

    b) Prepare 2 bottle of 20 ml P1 by using pipette

4. Process of preparation of P2

    a) Add 5 ml of PEDOT:PSS to one of 20 ml P1, stir well and label "P2"

    b) Add deionized water to another bottle of 20 ml P1, mix it and labelled "P1"

    c) Stir the bottles of P1 and P2 individually and observe any changes (Figure 23). Observation: By adding the PEDOT:PSS polymer solution, polymer solution changes from colourless and transparent into dark blue colour; and no sediment was seen.   Thus, it shown that PEDOT:PSS can dissolve into P1.

P1 & P2

Meta-aramid
Solution
P1

(P1 is made from
Normal meta-aramid polymerization Process)

Meta-aramid
Conductive Solution
P2

(Simply add PEDOT:PSS solution in to
Meta-aramid solution)

Figure 23: Transforming from P1 to P2.

4. Processing Experiment for F2 & F1

a) Using pipette to transfer 3 ml out of bottle P2 to make a layer on a 100 cm x 100 cm glass plate, put another 100 cm x 100 cm glass plate on the top to form the conductive meta-aramid film, F2

b) F2 is removed from glass plates

c) Process F2 with ultrasonic vibration for 30 minutes to eliminate bubbles and remaining solvent from original P2 mixture

d) F2 is then rinsed with deionized water to eliminate any residual

e) F2 is put into the vacuum oven for 2 hours at 100°C

f) Test F2 for electrical surface resistivity by four-point probe

g) F2 is then put into the oven again for 2 hours at 200°C and stage "f" is repeated

h) F2 is again put into the oven for 2 hours for 300°C and stage "f" is repeated. This process is repeated with P1 to produce F1 to enable comparison

5. Results

Table 13 shows comparison of meta-aramid F1 film and meta-aramid F2 (with PEDOT:PSS) film electrical resistivity data. All Measurements were over the measurement limit.

Table 13: Surface resistivity test per F1 and F2 after oven treatment for 100 °C, 200 °C and 300 °C

Temperature °C	Surface Resistivity Measurements Ohms/sq.									
	F1					F2				
	1	2	3	4	5	1	2	3	4	5
100	*	*	*	*	*	*	*	*	*	*
200	*	*	*	*	*	*	*	*	*	*
300	*	*	*	*	*	*	*	*	*	*
Remark: * Over the Surface Resistivity Meter Measurement										

a) Compatibility result

The experiment showed that PEDOT:PSS can be easily dissolved into the P1 meta-aramid polymer solution.   However, after 24 hours, the solution P2 showed separation between two different polymer solutions (Figure 24).

b) Water rinse result

It is concluded that in F2, fibrid film form, the conductive properties from PEDOT:PSS were washed away during the rinse water process.   As a result, when comparing the surface resistance testing results of F2 and F1, both displayed surface resistivity above four-point probe meter measurement.   The experiment shows that the meta-aramid fibrid failed to provide adequate adhesion for PEDOT/PSS.   It is concluded that PEDOT:PSS could not be integrated during the process of fibrid forming as PEDOT:PSS was washed away during rinse water process.

c) Temperature impact result

The temperatures treatment from 100°C to 300°C had no significant impact on the surface resistivity (Table 13).
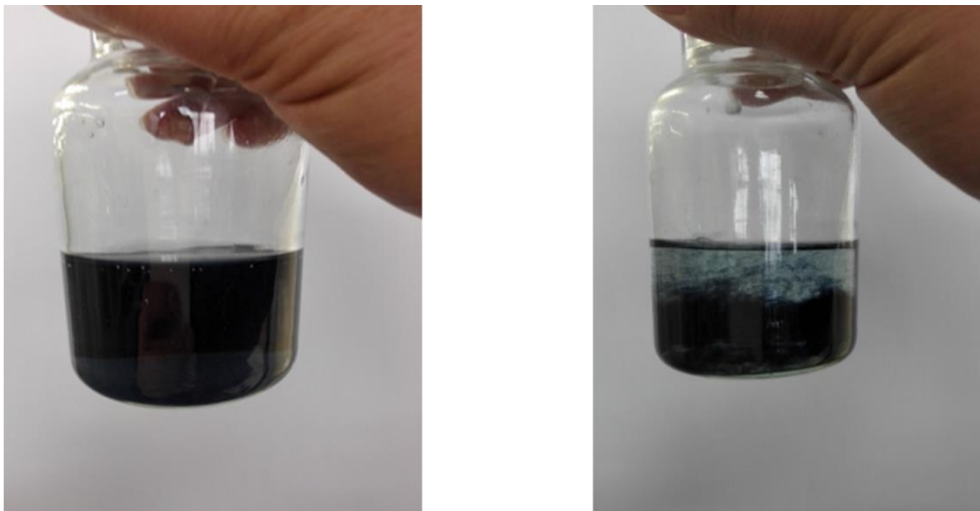
After 24 hours, P2 from dissolved state to separation state, it had shown that PEDOT:PSS had sunk to the bottom

Figure 24: P2 solution before (left) and after (right) 24 hours.

4.5.3 Preparation and Characterisation of Standard Papers B1 and C1 and PEDOT:PSS Coated Papers (B2 and C2)

B2 is B1 coated with conductive polymer solution PEDOT:PSS. The purpose of this experiment is to investigate the difference in conductivity after applying different levels of PEDOT:PSS. Two different basic weight grades of base paper are selected, 22 g/m^2 and 41 g/m^2 to compare any differences (Figure 25).

1. Material List

    a) 22 g/m^2 B1 base paper made from S1 and F1

    b) 41 g/m^2 B1 base paper made from S1 and F1

    c) PEDOT:PSS 1% wt.

    d) Deionized water 500 ml (pH: 5.0 - 9.0 and conductivity: $\leq$ 50 based upon X-Fiper testing procedures)

2. Equipment

    a) Glass 500 ml container

    b) Metal 500 ml container

    c) Weight scale with accuracy +/- 1 mg

    d) Pipette

    e) Vacuum oven

3. Experimental Process

    a) Prepare 10 pieces of 22 g/m^2 basic paper (B1), measure the weight

    b) Prepared 5 pieces of 41 g/m^2 basic paper (B1), measure the weight

    c) When calendered, both of 22 g/m^2 x 2 layers and 41 g/m^2 become the same thickness (0.05 mm) for comparison

    d) Measure the surface resistivity of all

e) Prepare 1.00%, 0.50%, 0.10%, 0.05% and 0.01% by diluting PEDOT:PSS liquid with deionized water in a 500 ml glass container labelled A, B, C, D and E respectively (Table 14), to enable minimization of PEDOT:PSS

f) Identify and mark the sample with B1 22 g/m^2 (A, B, C, D, E) and B1 41g/m^2 (A, B, C, D, E)

g) Dip B1 22 g/m^2 (A) base paper into PEDOT:PSS solution "A" for 5 sec.

h) Repeat step f and g, dip 22 g/m^2 base paper into PEDOT:PSS B, C, D, E solution

i) Repeat step f and g, impregnated 41 g/m^2 base paper into PEDOT:PSS A, B, C, D, E solution

j) Put all specimens into the oven with heat treatment/drying at 130°C for 10 minutes

k) Take out all specimens out of oven, cool down, measure the weight and record

l) Perform calendering process for all samples B2 (A-E) to become C2 (A-E)

m) 5 samples of all specimens are prepared in order to obtain reliable data. Average value has been taken surface resistivity and physical properties.

B2 and C2

Meta-aramid Base Paper B1 is made from S1 and F1 by paper making equipment

PEDOT:PSS

Meta-aramid Conductive Base Paper B2

(B2 is made by adding PEDOT:PSS)

Meta-aramid Calendering Paper C2

(C2 is made from B2 with calendering process)

Remark: B2: By adding PEDOT:PSS by impregnation process – color change from creamy white to blue
After calendering treatment, B2 become C2

Figure 25: Transforming B2 to C2.

Preparations for PEDOT:PSS solution:

Table 14: Solutions of PEDOT:PSS with deionized water

Preparation for PEDOT:PSS Solution			
Sample of B1 for	PEDOT:PSS in Weight (g)	Add Deionized Water in Weight (g)	PEDOT:PSS Solid Content in %
A	10	0	1.00
B	5	5	0.50
C	1	9	0.10
D	0.5	9.5	0.05
E	0.5	49.5	0.01

4. Results for papers with (B2, C2) and without PEDOT:PSS (B1, C1)

a) Surface resistivity

From Table 15, sample A surface resistivity average value is 410 ohms/sq. for 23 g/m² and 420 ohms/sq. for 40 g/m². Sample B surface resistivity average value is 16,200 ohms/sq. for 23 g/m² and 13,000 for 40 g/m². After base paper has been through the calendaring, the resistance surface value reduced by 2-4 times (Table 16). The plan sets the target surface resistance value is from 100 - 400 ohm/sq.; based upon the testing data, temperature or heat treated meta-aramid base paper, the surface resistivity is reduced. As a result, the target property performance is achieved with appropriate concentration of PEDOT:PSS at 1% (Sample A) for the basic weight of 40 g/ m².

b) Future work

The consideration of the future work shall be focused on the dispersion or impregnation process to ensure the uniformity of conductivity. This is because the standard deviation is over 20 and therefore not controllable for the production (Table 16).

c) Physical properties comparison of C1 and C2

The major property comparison between C1 and C2 shows no significant impact on the thickness, tensile strength and air permeability. The thickness has increased from 0.055 to 0.057 and the base weight has increased from 42 g/m^2 to 44 g/m^2 but still within the range or tolerance (Table 5, 36 g/m^2 to 44 g/m^2) within the designed specification (Table 17).

Base Paper B2 (A-E) with PEDOT:PSS Surface Resistivity

Table 15: Base Paper B2 (A-E) with PEDOT:PSS Surface resistivity

	Basic Weight g/ m² (AVG)	5 Trails of Surface Resistivity Measurement Ohms/sq.						
		1	2	3	4	5	Mean	Std D
A	23	400	300	500	400	450	410	66.3
	40	500	300	400	400	500	420	78.8
B	22	16,000	17,000	15,000	15,000	18,000	16,200	1166
	40	12,000	13,000	15,000	12,000	13,000	13,000	1095
C	23	*	*	*	*	*	*	*
	41	*	*	*	*	*	*	*
D	23	*	*	*	*	*	*	*
	41	*	*	*	*	*	*	*
E	23	*	*	*	*	*	*	*
	40	*	*	*	*	*	*	*
Remark: * Over the Surface Resistivity Meter Measurement								

Table 16: Conductive Calendering paper C2 measurement for the basic weight of 23 and 40 g/m²

	Basic Weight g/ m² (AVG)	5 Trials of Surface Resistivity Measuements C2 ohms/sq.						
		1	2	3	4	5	Mean	Std D
A	23	50	150	100	100	120	104	32.6
	40	100	120	120	160	150	130	21.9

Table 17: Compare test value for C1 and C2

Properties	Test Standard	Range	Unit	Target Value	Experiment Testing Value	
					C1	C2
Thickness	GB/T451.3-2002	0.048 - 0.065	mm	0.05	0.055	0.057
	ISO534					
	ASTM D374					
Basic Weight	GB/T45.1-2002	36-44	g/m^2	40	42	44
	ISO536					
	ASTM D646					
Tensile strength	GB/T12914	Machine Direction	N/cm	39	42	42
	ISO1924-2					
	ASTM D828					
Air Permeance (Schopper Method)	GB/T1667		um/ (pa*sec)	≤ 2	≤ 2	≤ 2
	ISO5636/2					
	TAPPI T 460					
Surface Resistivity			ohms/sq.	100-400	> 10,000	130

4.5.4 *Preparation and Characterisation of Paper B3*

B3 is produced from S2 and F1. Samples are compared to B1 and B2 in terms of surface conductivity. For the paper making process, the impact of dispersion after the PEDOT:PSS polymer solution is added into the meta-aramid fiber needs to be examined. (Figure 27)

1. Material List
   a) S2
   b) F1

2. Equipment
   a) Rapid Kothen Sheet Former

3. Experimental Process

   a) S2 conductive meta-aramid fiber is cut per to 6 mm to prepare sample paper (handsheet) in the laboratory.

   b) Handsheet paper is made via the mix of F1 meta-aramid fibrid and S2 meta-aramid fiber through the Rapid Kothen Sheet Former accordance with the general procedure (Figure 26).

Figure 26: Rapid Kothen Sheet Former (Tendringpacific, 2017).

   c) Dilute meta-aramid slurry 2 g with 7 liters of deionized water, then transfer diluted sample to the Rapid Kothen paper machine.   The filtrate was collected. Drying is done using the RK-dryer under vacuum at 95°C.   Base paper is formed. The surface resistivity is measured and recorded.

B3 and C3

Meta-aramid
Fibrid
F1
(Fibridation
Process)

Conductive
Meta-aramid
Fiber S2

Meta-aramid
Conductive
Solution
B3
(Making handsheet
paper by Rapid
Kothen sheet
former equipment)

Meta-aramid
Calendering Paper
C3

(C3 is made from
B3 with
calendering
process)
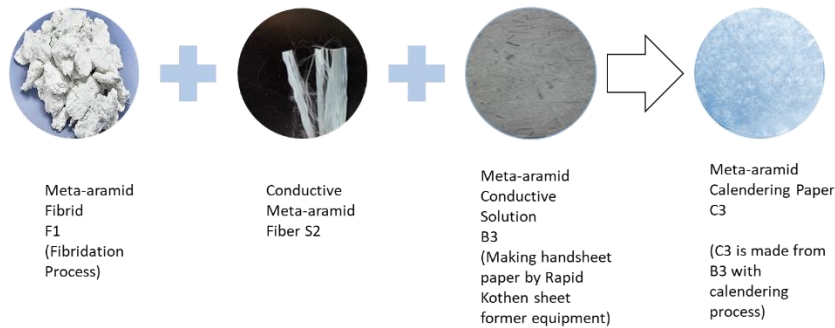
Problem: S2 has problem of fiber dispersion during hand-sheet making process, B3 has shown S2 is not evenly distributed
C3 surface resistance is out of the surface resistivity meter measure limit

Figure 27: The transform action of B3 to C3.

4.   Results

Base weight is measured (based on dry weight), in accordance with ISO 5269-2, resulting in sheets of 36-44 g/m^2.   The thickness is measured by ISO534 with the measurement from 0.047 to 0.065 mm.   The measurement of surface resistivity is 18,000 to 20,000 ohms/sq.   S2 had a surface resistivity measurement of 106 ohms/sq. as shown from Section 4.5.1.   The conductivity has dropped significantly.   It is concluded that since the surface resistivity has dropped, it is of no further interest and experiments are stopped.

4.5.5   *Investigating the Relationship between Coating and Conductivity for Papers between B2 and C2*

Based upon the Section 4.5.3 (B2 & C2 experimental testing result), further investigation is done to observe the impact of increasing the PEDOT:PSS coating size. The coating process is simulated using a paintbrush rather than dipping in the laboratory

to apply PEDOT:PSS onto the surface of the base paper. Finally, all samples go through a calendaring process to observe the impact after calendaring.

1. Material List

   a) B1

   b) PEDOT:PSS as supplied

2. Equipment or Parts

   a) Paintbrush

   b) Weight Scale with accuracy of +/- 1 mg

3. Experimental Process

   a) Measure the base paper basic weight

   b) Coat PEDOT:PSS on to the surface of base paper B1 become B2 conductive meta-aramid base paper

   c) Put B2 into the oven for 100°C for 10 minutes

   d) Measure the surface resistivity

   e) Repeat step b to d with additional coating to prepare (A), (B), (C), B1(D)

   f) Perform calendaring for all samples (A), (B), (C), (D) to become specimens of meta-aramid conductive paper C2 (A), C2 (B), C2 (C), C2 (D)

   g) Measure the surface resistivity for C2 (A), C2 (B), C2 (C), C2 (D)

   h) Simulate the water wash process on samples of C2 (A), C2 (B), C2 (C), C2 (D)

   i) Repeat the above process to obtain 5 specimens of all samples

4. Results

Table 18: Experiments on additional layers of PEDOT:PSS was brushed on B1 meta-aramid base paper

Base Paper B2 with different layers of coating								
5 Trails of Surface Resistivity Measurement Ohms/sq.								
No of Layers	Specimen	1	2	3	4	5	Mean	STD Deviation
1	(A)	800	1100	920	900	1200	984	145
2	(B)	350	450	300	500	400	400	70
3	(C)	200	100	250	300	120	194	76
4	(D)	10	11	80	80	20	40	33

a) Surface resistivity

This experiment clearly shows that extra coating increases conductivity. The mean surface resistivity data shows a reduction from 984 ohms/sq. to less than 40 ohms/sq. (Table 18). After the calendering, the surface resistivity was reduced. For only one layer of coating C2 (A), the surface resistivity was reduced from 984 ohms/sq. to 264 ohms/sq. The remaining meta-aramid conductive paper samples of C2 (B), C2 (C), C2 (D), the surface resistivity was less than 100 ohms/sq. It is concluded that additional layers of PEDOT:PSS could increase the conductivity, and after the calendering is done, the conductivity is increased (Table 19).

Table 19: Experiments on additional layers of PEDOT:PSS was brushed on C1 meta-aramid calendering paper

Calendering Paper C2 with different layers of coating								
		5 Trails of Surface Resistivity Measurement Ohms/sq.						
No of Layers	Specimen	1	2	3	4	5	Mean	STD Deviation
1	(A)	250	300	280	230	260	264	24.2
2	(B)	60	80	90	80	70	76	10.2
3	(C)	20	25	60	80	20	41	24.6
4	(D)	0	0	21	25	10	11	10.4

b) Water rinse result

The conductive properties from PEDOT:PSS remained after the rinse water process for samples of C2 (A), C2 (B), C2 (C), C2 (D) (Table 20). It is concluded that he conductivity measurement of surface resistivity exhibited no significant changes.

Table 20: Surface resistance of calendering paper C2 (A) after water rinse

Calendering Paper C2 After Water Rinse								
		Surface Resistivity Measurement Ohms/sq.						
No of Layers	Specimen	1	2	3	4	5	Mean	STD Deviation
1	(A)	240	320	260	250	280	269	25.9

4.5.6 Preparation and Characterisation of Calendered Paper with application of PEDOT:PSS Ink (C4)

Formulate the ratio of PEDOT:PSS to be integrated into the meta-aramid final paper C1 to obtain the best product after calendaring is performed. The aim is to identify the impact of integration of PEDOT:PSS after calendering in terms of surface resistivity, tension strength and so as the air permeability.

1. Material List

 a) C1

 b) Orgacon® PEDOT:PSS ink version as supplied

2. Equipment

 a) Print brush

3. Experimental Process

 b) Apply calendaring process to form C1

 c) Prepare PEDOT:PSS ink version

 d) Apply PEDOT:PSS ink version to the C1 with print brush

 e) Measure the surface resistivity and record

4. Results

Based upon the experiments, the conductivity or surface resistivity of C4 can meet the original design requirements (Table 21), it has shown no significant impact on the base weight, tensile strength and the permeability compared to the normal meta-aramid paper (Table 21, 22).

Table 21: PEDOT:PSS Ink Version C4 with 5 specimens

Calendering Paper C4 with Ink Version PEDOT:PSS							
Test Item	1	2	3	4	5	Mean	STD Deviation
Thickness (mm)	0.056	0.058	0.062	0.056	0.055	0.057	0
Basic Weight (g/m²)	43	44	44	45	44	44	0.6
Tensile Strength (N/cm)	41	42	42	43	42	42	0.6
Surface Resistivity (ohms/sq.)	190	150	130	105	175	150	30

Table 22: Summary results for C1, C2, C4

Properties	Test Standard	Range	Unit	Target Value	Experiment Testing Value		
					C1	C2	C4
Thickness	GB/T451.3-2002 ISO534 ASTM D374	0.048–0.065	mm	0.05	0.055	0.057	0.057
Basic Weight	GB/T45.1-2002 ISO536 ASTM D646	36–44	g/m²	40	42	44	44
Tensile strength	GB/T12914 ISO1924-2 ASTM D828	Machine Direction	N/cm	39	42	42	42
Air Permeance (Schopper Method)	GB/T1667 ISO5636/2 TAPPI T 460		um/ (pa*sec)	≤2	≤2	≤2	≤2
Surface Resistivity			ohms/sq.	100–400	>10,000	130	150
Flame Retardant	UL 94			V-0	Gate 5	Gate 5	Gate 5
Rohs				Required	ok	ok	ok
REACH				Required	ok	ok	ok
Electrical Insulation System	UL 1446		°C	>/= 200	Gate 6	Gate 6	Gate 6
The target price is set less than the competitor at 30 to 50%							

Based on these results C1 and C2 specimens were investigated for thermal and mechanical properties, differential scanning calorimeter (DSC), infrared spectroscopy for material identification (FTIR), thermogravimetric analysis (TGA).

4.5.7   *Infrared Spectroscopy for Material Identification (FTIR)*

The test was performed at the Weipu Jishu Testing Laboratory. The FTIR test was selected as the preferred method in order to identify and compare the normal type of meta-aramid paper C1 against conductive meta-aramid paper C2, so any variation in chemical bonds and molecular structure can be identified.   Two scans were made with the conclusion that have all of the same absorption valleys and peaks with a slight difference in the magnitude in the lower frequency end (right hand side) of the scans. The analytical spectrum produced is compared in a reference library to a normal type of meta-aramid paper to identify components or to find a "best match" for any unknown materials, using the catalogued spectra for known materials.   Results are presented in Figure 28.
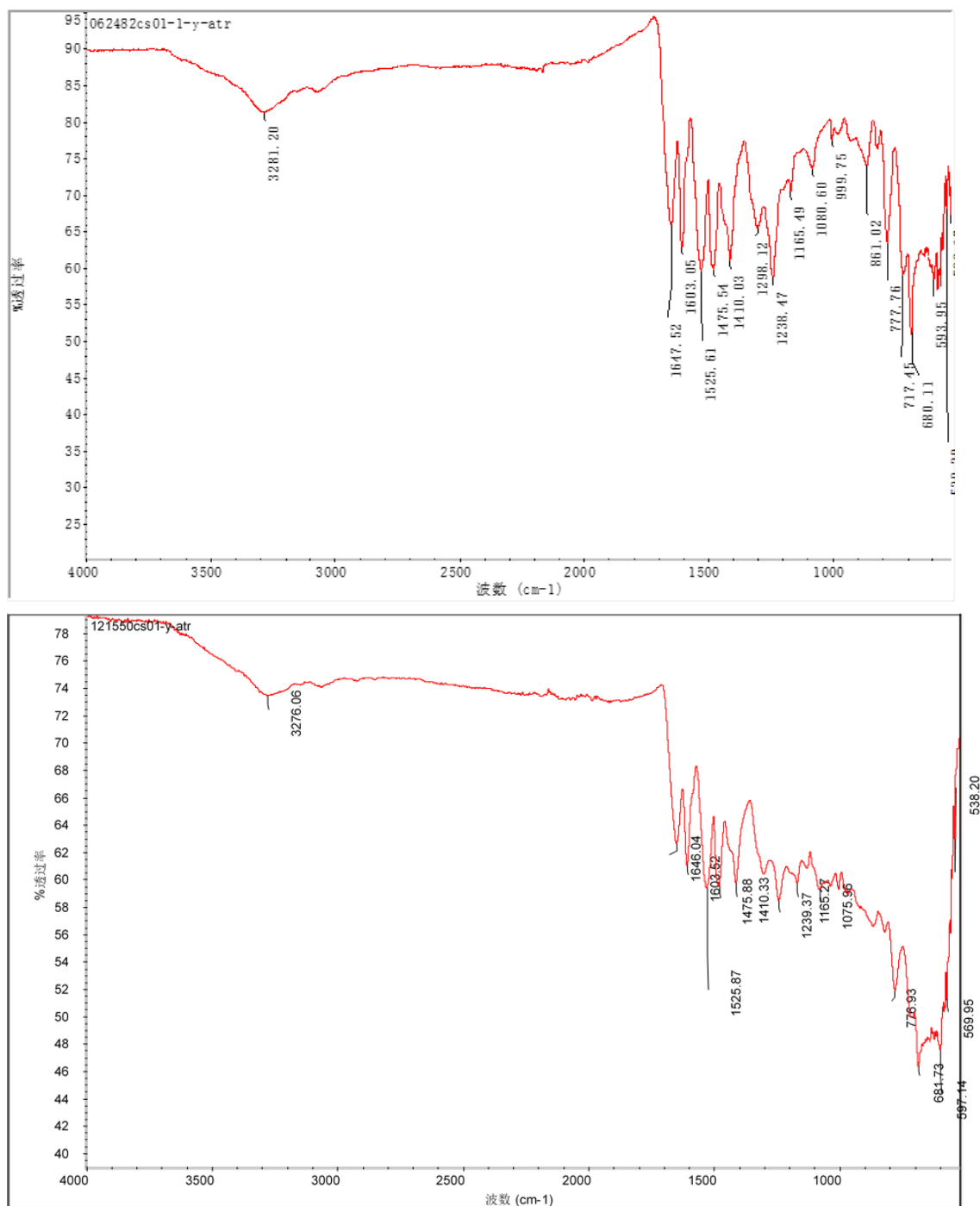
Figure 28: Infrared spectroscopy for material identification (FTIR) for sample of C1 (top) and C2 (bottom).

1. Results

Based upon the comparison in Figure 28, the top graphic represents normal type of meta-aramid paper C1 and the bottom graphic represents C2 conductive meta-aramid paper. The comparison of the two FTIR scans show the same absorption patterns in

both C and C2 throughout the full spectrum.   There is observable difference in the magnitude of the absorption peak and valley patterns in the frequency range between approximately 1200 and 500 cm^{-1}.   For example, PEDOT:PSS It is expected to see peaks around 1350 cm^{-1} which are the C-C and C=C bonds of the thiophene ring.   Peak at 1230 cm^{-1} is the C-O-C stretching in the ethylenedioxy group. This identifies the PEDOT component (1).   PSS is recognized by the S=O and S-phenyl bonds (at 1300 cm^{-1} and 100-700 cm^{-1}) (2) (Glagovich, 2005). When compares this region published spectrum of PEDOT:PSS, it confirms the presence of PEDOT:PS on the C2 sample (Figure 29).   Two additional tests were subsequently performed; DSC and TGA to further evidence the presence of PEDOT:PSS.
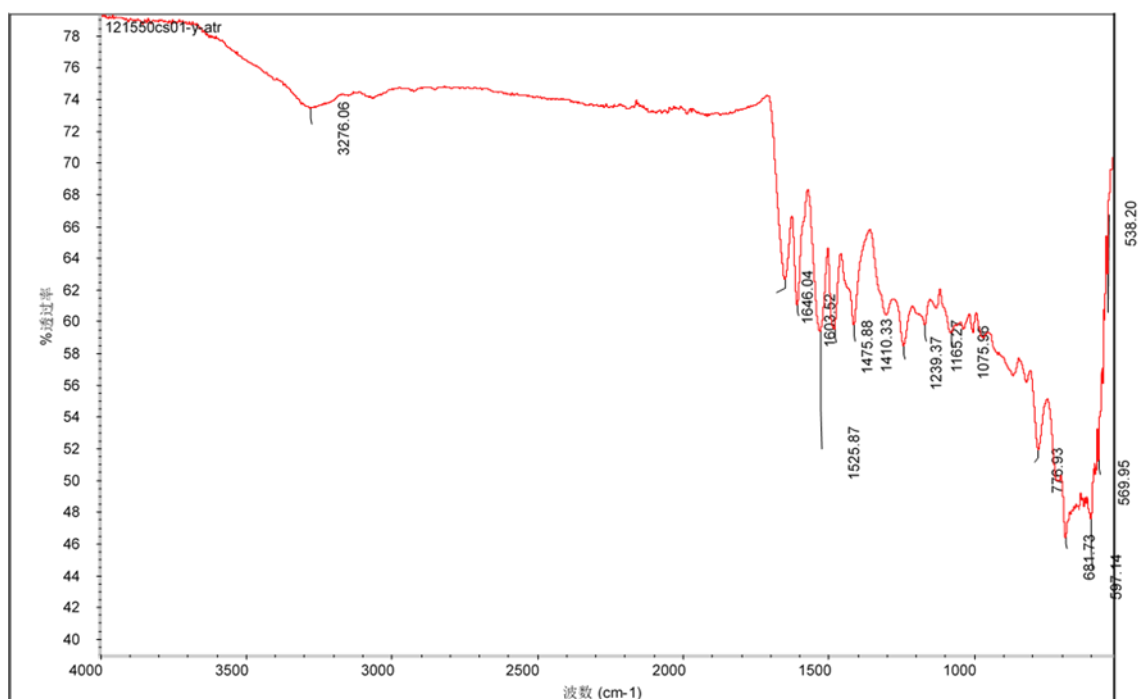
Figure 29: Infrared spectroscopy for material identification (FTIR) for sample of C2 (top) and PEDOT:PSS (bottom).

4.5.8 *Differential Scanning Calorimetry (DSC)*

DSC measures the difference in the heat flow to a sample and to a reference sample as a direction function of temperature under heating. It is necessary to undertake DSC to confirm that incorporating PEDOT:PSS chemical retains the heat stability of the meta-aramid paper.

Figure 30 shows tests for C1 and C2. It should be noted that the X-axis showing the heating temperature is on the same scale for both C1 and C2; the Y-axis is not on the same scale due to differences in peak size.

The scan for C1 shows a peak around 100°C, likely to be water evaporation but there is an additional peak in the C2 sample starting at around 222°C this can be assumed to

85

be the PEDOT:PSS when compared to C1. This is well know that it is difficult to measure PEDOT:PSS. (Govindaiah; *et al,* 2015)

There is no indication of decomposition of either C1 or C2 at temperatures out to 300°C in either scan.   This indicates the performance of C1 and C2 can be expected to be the same.
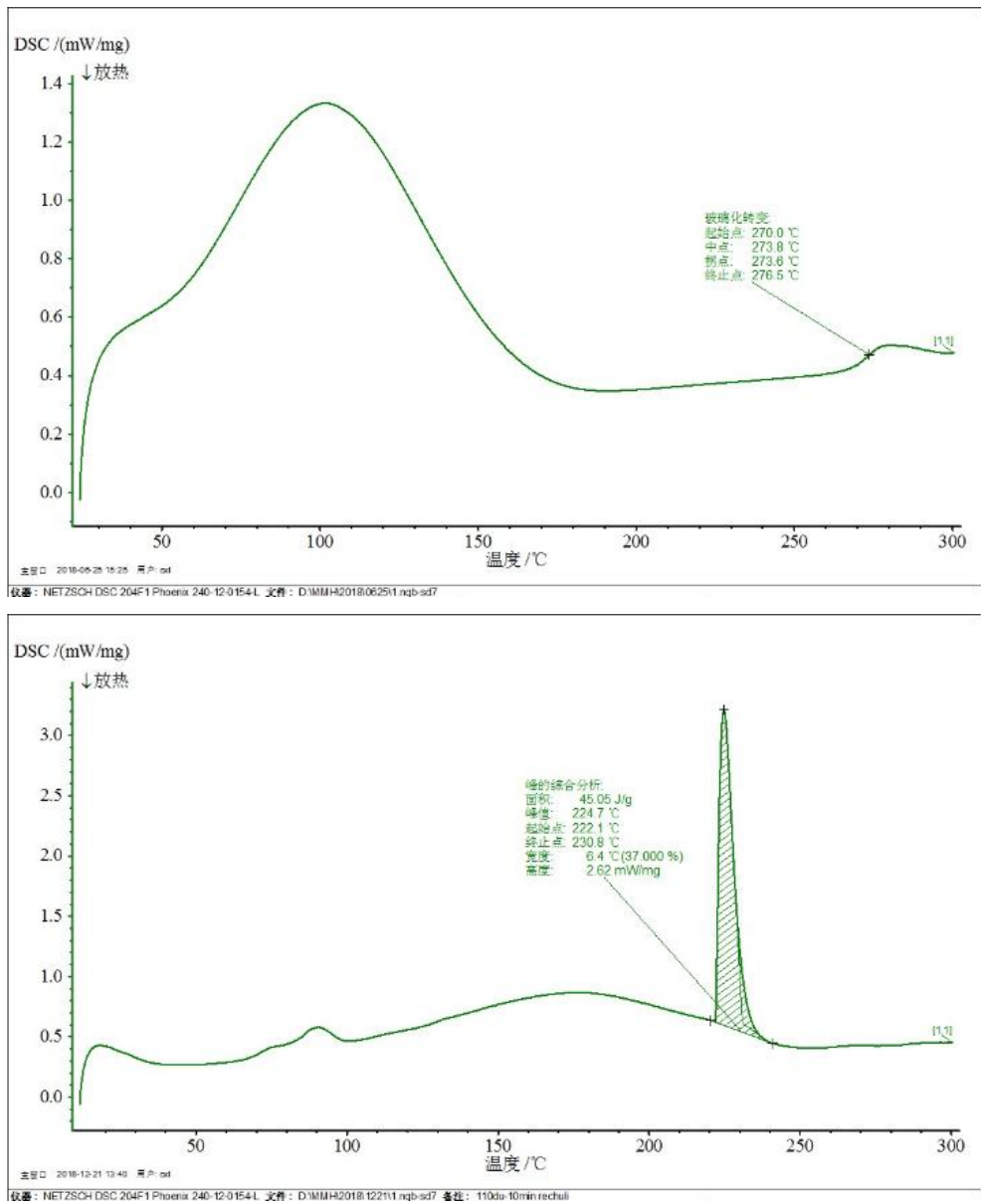
Figure 30: C1 (top) and C2 (bottom) DSC.

4.5.9 The Thermogravimetric Analysis TGA

The TGA thermal curve indicates a weight loss occurring across the temperature range. Again the patterns of C1 and C2 are very similar to each other. Both show weight loss starting as soon as heat is applied. Again, due to the hydroscopic nature of the chemistries of the specimens, the initial weight loss is removal of bonded water molecules. Across the entire test temperature range the pattern of weight loss of both samples is similar. (Figure 31)
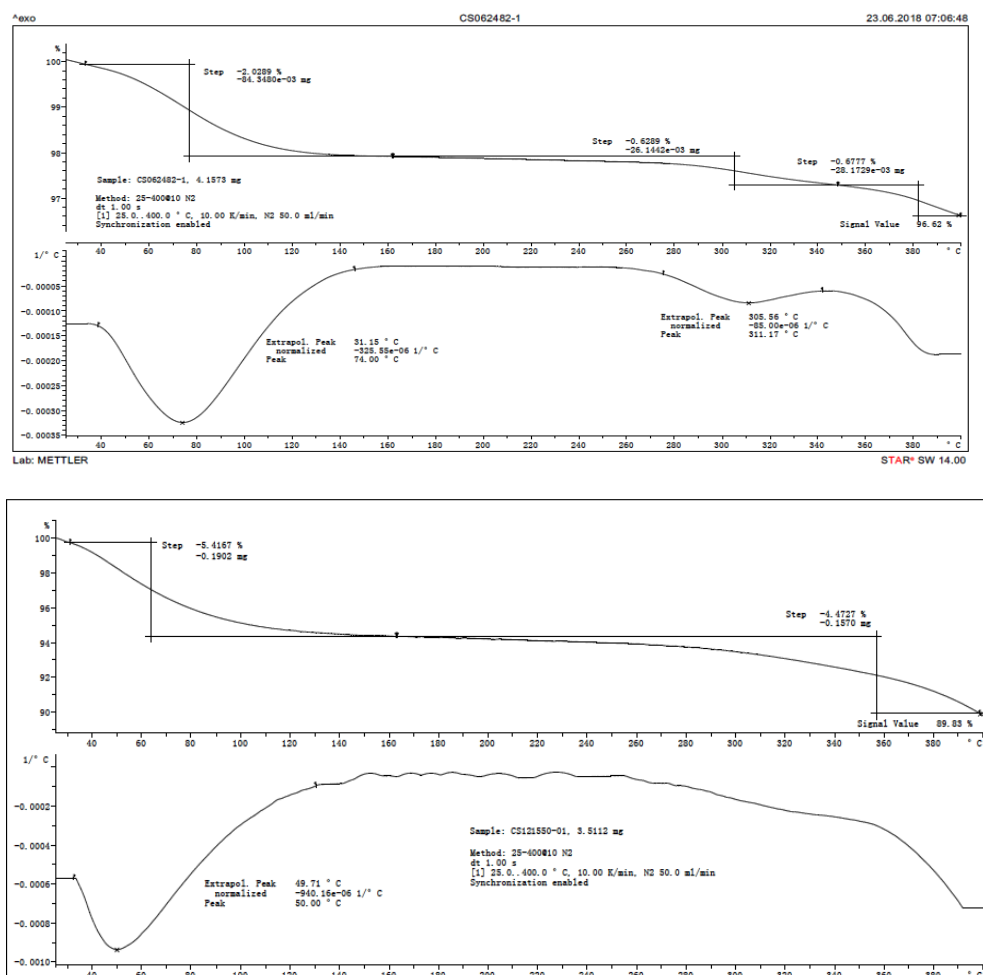
Figure 31: C1 (top) C2 (bottom) The Thermogravimetric Analysis TGA (Temperature versus weight loss).
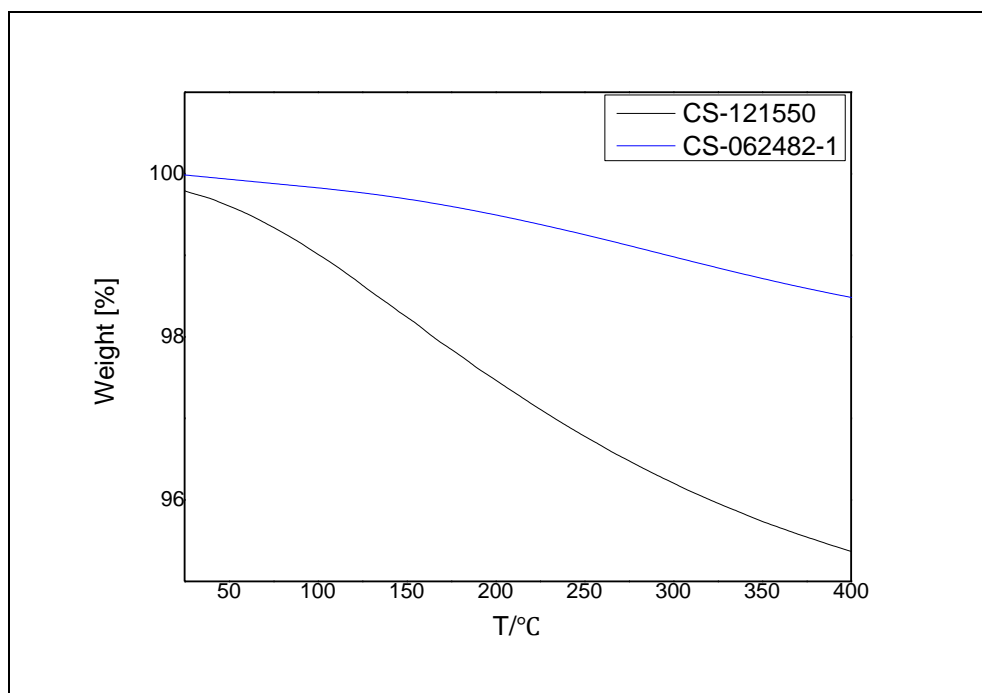
Figure 32: Weight loss blue line represent C1 and black line represent C2.

Samples C1 and C2 have the same basic molecular structure and can be expected to provide similar long heat stability performance. However, incorporation of PEDOT:PSS is suggested to show limited weight loss relative to C1 (Figure 32). There is the possibility that incorporation of PEDOT:PSS into the base paper sample only could improve the stability of the PEDOT:PSS components.

In conclusion, the results of the three analytical tests fit the criteria in IEC 661858-2 as an allowable confirmation of substitution of C2 for C1 in high voltage form-wound rotating machinery in IEC 60034-18-31.

4.6 Material Properties

C1 (normal meta-aramid paper) and C4 (conductive meta-aramid paper) shows no significant differences in the thickness, tensile strength or air permeability properties (Table 20 and 21). The base weight of C2 and C4 has increased compared to C1 but

is still within the range or tolerance of the design specification (Table 22).   C4, the PEDOT:PSS coating agent containing ink and other additive, requires further evaluation to confirm how these additives may affect the end-user application. PEDOT:PSS ink version has a higher viscosity as per manufacturers specification that can only be applied on one side using a printer method.   It is unclear what the impact of application to both sides will have on how uniformity can be maintained.   During the water washing process, it exhibited increased tackiness to touch when compared to the water version.

In conclusion: the goal of these experiments is achieved based upon the current data and finding.

4.7 Discussion

The overriding purpose of this study was to determine the possibility and processes of bringing together two extremely different types of polymers conductive and non-conductive to form a conductive material.   To accomplish this goal, it was necessary to develop a new material prototype, which is capable of relaxing an electric field generated between a coil and an insulation material.   The new material needed to have some conductivity and at the same time, it was required to be highly heat-resistant. Thus, meta-aramid paper integrated with a conductive polymer solution became the choice of solution.   PEDOT:PSS was the selected conductive polymer.   The testing data collected in the experimental sections show that the coated aramid material exhibits conductive behaviour with a surface resistivity measurement of 100 to 400 ohms/sq.   The goal of retaining the thermal and mechanical properties and enhancing the conductivity is achieved based upon the current data and finding (Figure 33).   As presented in Table 22, no significant difference in tensile strength and permeability between normal type of meta-aramid paper and conductive type of meta-aramid paper

was found.   Loading of less than 1% wt. PEDOT:PSS on the meta-aramid materials, did not appear to significantly affect construction of either meta-aramid fiber and meta-aramid fibrid and paper.   If the mechanical structure has been affected during the paper making and calendaring process, the mechanical strength of tensile strength would likely have been influenced (Table 22). The processability and stability are now discussed separately.

After PEDOT:PSS is coated, the thickness has increased from 0.055mm to 0.057mm and the basic weight has increased from 42 g to 44 g

PEDOT:PSS

Meta-aramid Paper

Conductive Meta-aramid Paper
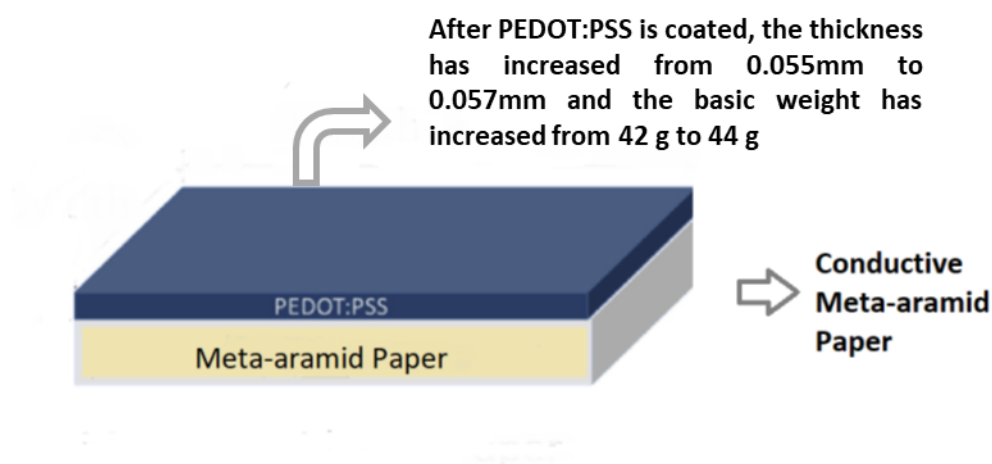
Figure 33: **C2 -** Thickness and basic weight are increased after PEDOT:PSS is coated and treated calendering.

4.7.1   *Processes involving Water Wash Treatment*

Based upon the lab experiment work from Section 4.5.1, it was possible to process S2 via the normal process route and adding the PEDOT:PSS per coating method in the laboratory.   A challenge was that the water washing process during the mixing of S2 with F1 to form a paper B3 and C3, (Section 4.5.4) caused the PEDOT:PSS to be washed out.   The surface resistivity of S2 is 106 ohms/sq.; however, after the washing process was applied to the S2 specimen, the surface resistivity was increased to the level that could not be detected (insulation properties).   Furthermore, (Section 4.5.2) using conductive fibrid aramid film F2, two dimensional films were formed.

Applying the water treatment one to four times affected the conductivity.   A similar finding was found from the experimental work on B3 and C3, forming the base paper B3 by using conductive meta-aramid fiber S2 through the RK-dryer sheet former. The surface resistivity increased to such a level that it was unable to be measured by the four-point probe meter.   As a result, it was determined that it is necessary to avoid water treatment right after PEDOT:PSS 1% wt. is added in any conductive meta-aramid paper process.   Based upon the experiments in Section 4.5.1 and 4.5.2 and 4.5.4, the impregnation method of coating PEDOT:PSS on the fiber and integrating PEDOT:PSS to the fibrid might not be the solutions for this project.

4.7.2   *Processes Involving Heat Treatment*

With regards to conductive meta-aramid base paper B2 and C2, after the conductive meta-aramid base paper B2 goes through the calendaring process (by heating the materials over 250°C by hot rollers with approx. 25 Meters/minute), the conductivity was increased as the surface resistivity was reduced 2 to 3 times. The temperature of the calendering process is higher than the glass transition temperature of meta-aramid and close to the crystallization temperature of meta-aramid.   The calendering process not only enhanced the mechanical strength, but also brought the materials constituting the conductive aramid paper into close and firm contact with other.   According to the Section 4.5.3 Table 15, 1 % of PEDOT:PSS is chosen as optimal.

Comparatively, the conductivity of calendered paper C2 is much better than the conductive base paper B2.   At high temperature, the fibrid undergoes a softening process which enables it to have excellent adhesion between the fibers and the PEDOT:PSS under the calendering process condition.   The DSC shows (refer to Section 4.5.8) that PEDOT:PSS polymer has been integrated into the paper structure. It is confirmed that integrating the water based version of PEDOT:PSS right after the

base paper is formed and before calendaring process is done, is the favourable solution based upon current research data.

4.7.3   *Increased Conductivity*

According to the experimental results, the conductivity can be adjusted by two different methods.   One is to increase the percentage of conductive polymer content; the other is to increase the conductivity by additional layer coating.   B1 and B2 were coated with PEDOT:PSS from 0.01% (0.5 g) to 1.0% (5 g).   Sample C2 is the calendered version of B2 and therefore was also available in the range of 0.01 to 1.0 % PEDOT:PSS. (Table 15) indicated that 0.7% (above 2.5 g) of PEDOT:PSS coated on the base paper could provide sufficient conductivity to meet the product specification.   As the base paper B2 went through the calendering process, the conductivity was increased meaning the surface resistivity was reduced 2 to 3 times.   In order to provide a safety tolerance a decision is made to use a minimum concentration of PEDOT:PSS at 1% for the basic weight of 40 g/m².

After the base paper B2 went through the calendaring process, the conductivity was increased so while the surface resistivity was reduced 2 to 3 times.   Due to the calendering process involving the temperature higher than the glass transition temperature of meta-aramid and the calendering process close the crystallization temperature of meta-aramid, it has integrated PEDOT:PSS polymer into the meta-aramid paper structure.

In the experiment in Section 4.5.2, which mixed two different types of polymer solutions of PEDOT:PSS polymer solution and meta-aramid polymer solution, it was illustrated that the PEDOT:PSS conductive polymer solution could be easily dissolved in the meta-aramid solution.   When the mixed solution was retained for 24 hours, the

results showed that the two polymer solutions separated (Figure 24). As a result, additional procedures must be considered to retain stability during the storage and processing. For example, agitation and tank life needed to be considered to monitor the stability of PEDOT:PSS solution during the process.

Application of additional layers of PEDOT:PSS is another alternative way to increase the conductivity. Results obtained from Section 4.5.3 between B2 and C2, (See Table 15 & 16) suggest that additional layers of coating increased conductivity. The surface resistivity reduced from 984 ohms/sq. to less than 100 ohms/sq. Therefore, this suggests conductivity can be tailored by controlling an additional layer process.

Overall, the hypothesis of integrating the PEDOT:PSS with meta-aramid to provide a conductive meta-aramid paper can be realized by the prototypes of C2 and C4, which demonstrated the achievement of the initial specification (Table 22) specific request on tensile strength, air permeance and the surface resistivity. The tensile strength can be reached per requirement of 39N/cm and the air permeance is met as it is less than 2 µm/Pa.s. The surface resistivity is within the range requirement of 100 to 400 ohms/sq. The innovative conductive meta-aramid paper can then be applied directly to the slot portion of conductor bars by a wrapping process. Because of its conductivity, it can equalize the voltage over the length of the conductor bars surface to guarantee a homogeneous distribution of electrical field in the ground wall. However, this is yet to be proven in service conduction.

4.8 Production Trials
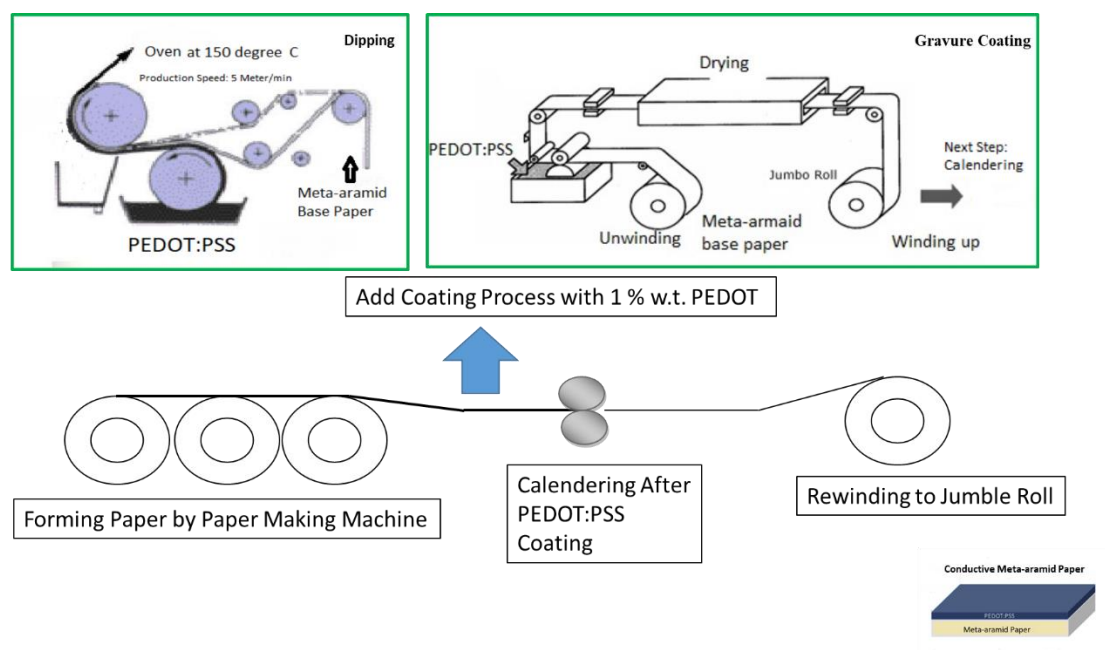
Figure 34: Adding coating procedures (dipping & gravure) before calendering.

X-Fiper scale-up trials are performed on existing production lines and mainly use two different applications: dip coating and gravure coating (Figure 34).   To ensure repeatability, assessment of results over time and by different operators following the procedures are documented.   In order to limit the number of trials, a general factorial design with three replicates was selected.   Three production trials with two different coating method are implemented.   PEDOT:PSS (as supplied 1 % w.t.) is coated after meta-aramid base paper is formed, the coating is added before calendering.

4.8.1   Dipping Process

Dipping is the fastest application method and the automated equipment is better than manual processes. In this simple process, the meta-aramid base paper is dipped into a bath of the PEDOT:PSS, which is normally of a low viscosity (35 mPas) to enable the coating to run back into the bath as the substrate emerges (Figure 35).   To prepare the conductive paper production run, 3 rolls of the 1000 mm x 300 M x 41 g/m^2 base paper

are used. Three repeat trials are run to gain repeatability data. 1 % w.t. of PEDOT:PSS solution is prepared for the coating equipment. The coating equipment is cleaned based upon the X-Fiper cleaning procedures SOP and FOD SOP. The coating process parameter is set with the speed for 5 (5-30) meters per minute standard operating procedures and the oven temperature at 150°C. In practice, the coating speed parameter is limited by the oven.
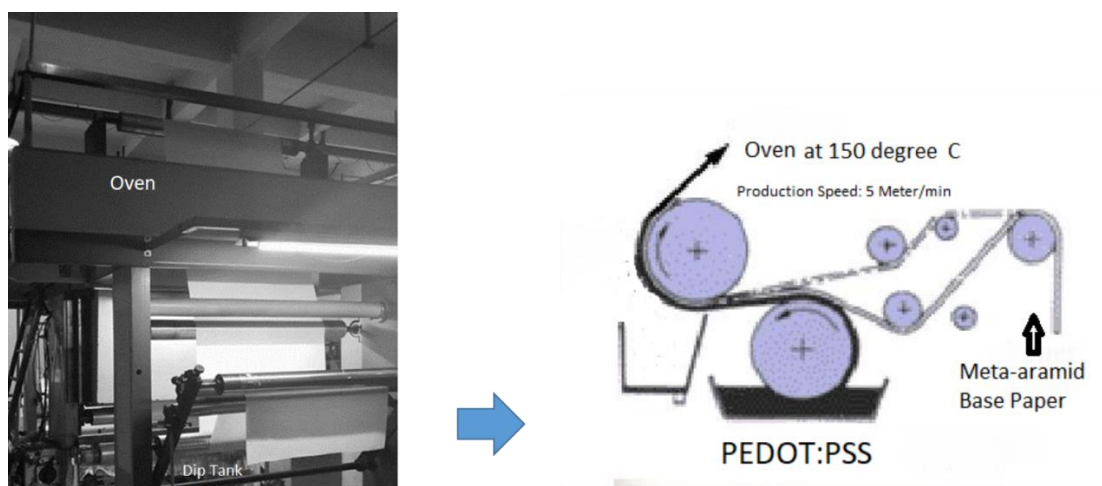
Figure 35: Dip coating equipment and process.

Process observation: bubbles in the form of trapped air are seen within the PEDOT:PSS coating. After calendering, pinholes are still visible on the surface calendering paper.

Result: The standard deviation of resistivity result is high reflecting that the coating uniformity needed to be improved. The result of 5 readings are presented in Table 23. Five readings are measured over one meter of sample.

Table 23: Testing result from 3 repeated trials

Trial No.	Surface Resistivity Measurements Ohms/sq.					Average Value
	1	2	3	4	5	
1	325	310	564	237	231	333
2	123	423	250	213	321	266
3	231	150	245	147	240	203
Mean						267
Coefficient Std. Deviation						20%

Problem identification:

Before calendering, the meta-aramid paper is porous with an uneven, rough surface. A fluff problem exists on the surface of the meta-aramid base paper, which causes the burrs to be generated in the subsequent trial coating process; therefore, leading to unstable coating uniformity. Furthermore, in the process of dipping coating, bubbles occurred during the rapid contact between the meta-aramid base paper and PEDOT:PSS solution that also resulted in uneven dispersion of PEDOT:PSS on the meta-aramid base paper surface.

Solutions:

a) Two approaches can be taken either (1) improve the surface smoothness of meta-aramid paper or (2) consider changing the coating method. Pre-heated treatment on the base paper before PEDOT:PSS coating might be a consideration.

b) Coating method: Air entrapped under meta-aramid base paper by the coating process can be forced out during the curing process and cause bubbles. Consider coating equipment with added brush coating to blend the PEDOT:PSS so it flows easily and "flow" the material onto the meta-aramid base paper. Further

investigation is needed to be done for the coating process. The coating process development is not considered priority at this point.

4.8.2   Gravure Coating & Multi-layers

The gravure coating method relies on an engraved roller running in a coating bath, which fills the engraved cell of the roller with PEDOT:PSS solution. The excess coating on the roller is wiped off by the doctor blade and the coating is then deposited onto the meta-aramid base paper as it passes between the engraving roller and a pressure roller. (Figure 36)
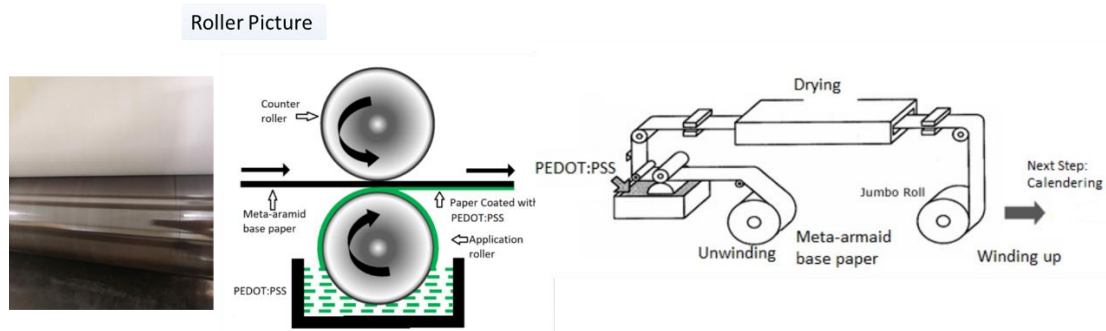
Figure 36: Gravure Coating Process.

To prepare the conductive paper production run, 6 rolls of the 1000 mm x 300 M x 41 g/m^2 base paper are used. Three repeat trials per part no. of engraved 110 and engraved 180 (engraved 180 will have less pick up compare with engraved 110 as engraved density is higher) were run to gain repeatability data. 1 % w.t. of PEDOT:PSS solution is prepared in the coating equipment. The flow condition near the contact point between PEDOT:PSS and the upper roll was associated with some coating defects (air entrainment) owing to the material parameters (surface tension) and the inlet feed condition. Most serious coating defect, is likely to occur with high coating speeds. Further optimization will be required.

Result:

1. Table 24 (by using engraved roller with part no. of 110) and Table 25 (by using engraved roller with part no 180) show the surface resistivity measurements. The uniformity is improved but the conductivity has still not met the requirement.

Table 24: Surface resistivity measurements (engraved 110)

Engraved lines 110 Trial No.	Surface Resistivity Measurements Ohms/sq.					Average Value
	1	2	3	4	5	
1	1023	1097	962	1031	987	1020
2	1002	1080	1022	980	1000	1016
3	1020	1125	970	1020	980	1023
Mean						1020
Coefficient Std. Dev.						4.5%

Table 25: Surface resistivity measurements (engraved 180)

Engraved lines 180 Trial No.	Surface Resistivity Measurements Ohms/sq.					Average Value
	1	2	3	4	5	
1	3454	3349	3485	3412	3469	3434
2	3350	3400	3330	3450	3500	3406
3	3420	3380	3415	3490	3470	3436
Mean						3425
Coefficient Std. Dev.						1.5%

By using this second coating process for meta-aramid base paper and PEDOT:PSS, the coefficient standard deviation of surface resistance value is reduced to less than 5%. The PEDOT:PSS pick up is not enough; therefore, additional layers might be considered.

2. Cause analysis and improvement

At present, the paper needs to be coated twice to ensure the consistency of surface conductivity. In order to obtain a homogeneous coating with sufficient conductivity and adequate sealing of the paper surface, the coating layer has to fuse thoroughly and anchor to the base paper. Furthermore, aqueous PEDOT:PSS coatings "dry" by removal of water from coating solids. This typically happens through evaporation and through absorption into the paper itself. Several factors affect the time it takes before the paper is dry including drying equipment, drying time and operation speed.

3. Future work

Additional coating is required including the following condition:

- Select the right engraved roller to increase the amount of PEDOT:PSS to be pick up
- Oven criteria needs to accommodate the reduction of the curing time in the curing process
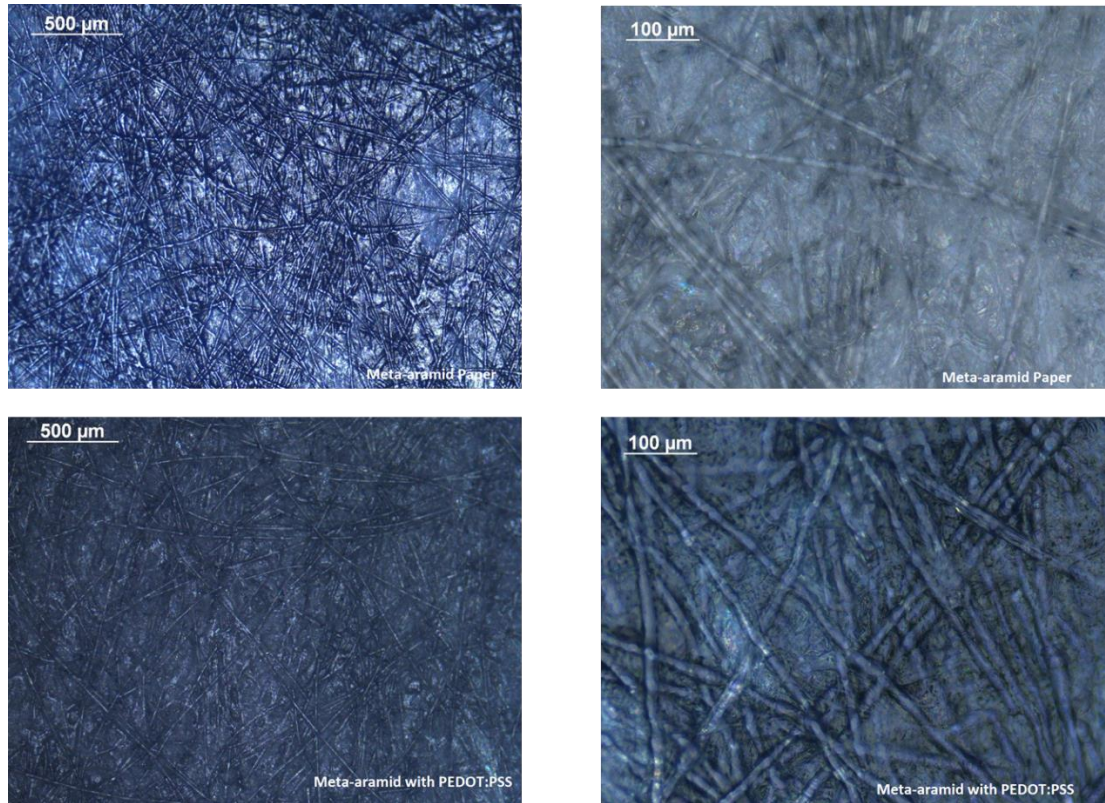
Figure 37: Optical microscopy for meta-aramid paper (top) and meta-aramid paper with PEDOT:PSS (bottom) 100 µm and 500 µm.

Figure 37 shows optical microscopy on the meta-aramid paper which was carried out for comparison purposes. The images show that PEDOT:PSS appeared to have no impact on the visible paper structure that was also reflected in the mechanical properties being unchanged.

4.9 Comparison with Competitor Materials

Comparing the prototype sample with the competitor materials, the physical properties of tensile strength and the electrical properties of surface resistivity are very close (Table 26). One of the criteria of gate 4 is met and gate 5 is opened to allow production trial in the production run. Production trial sample is then ready for future customer application validation in terms of the compatibility with the impregnated resin and the system thermal aging.

Table 26: Comparison of competition specification

	Specification		Average Testing Value
	Unit	DuPont T843S	New Developed Product
Nominal Thickness	mm	0.05	0.05
Basic Weight	g/m^2	38.5	40
Tensile Strength MD	N/cm	50	47
Surface Resistivity	Ohms/sq.	100-300	100-400

4.10 Customer Screening of Prototype

Prototype specification and target price had been sent to three customers including Voith Hydro (Voith Hydro. 2009), Von Roll China (Von Roll) and Suzhou Better Technology Co., Ltd. (Suzhou Better) as both Von Roll and Suzhou Better Technology Co., Ltd. are X-Fiper current customers for meta-aramid paper. Von Roll had run the physical, electrical properties test based upon the X-Fiper R & D specification. General Manager and Operation in Charge from Von Roll gave feedback to X-Fiper that major physical properties of conductive paper including basic weight, tensile strength, and surface resistivity are met. The surface conductivity is within their requirement. However, the visual check of uneven colour and the surface resistivity measurement reflected that the coating uniformity needed to be improved. They expressed that once X-Fiper provide production trial sample, application test including wrapping on the conductor compatibility test will be performed. Suzhou Better Technology Co., Ltd. technical manager expressed the interest of this conductive meta-aramid paper as the reference price is much lower than their current purchase price. Yet Suzhou Better Technology Co., Ltd. looked for more information in terms of understanding actual performance in application of wrapping the conductor. Sample of 12 mm x 200 M is requested to be provided. With these input from customers, stage 5 gate is open to prepare the trial production run and go to customer validation stage. Validation from customer are to be as extensive as necessary to meet the needs of their intended application. Figure 38 exhibits the customer validation time line.
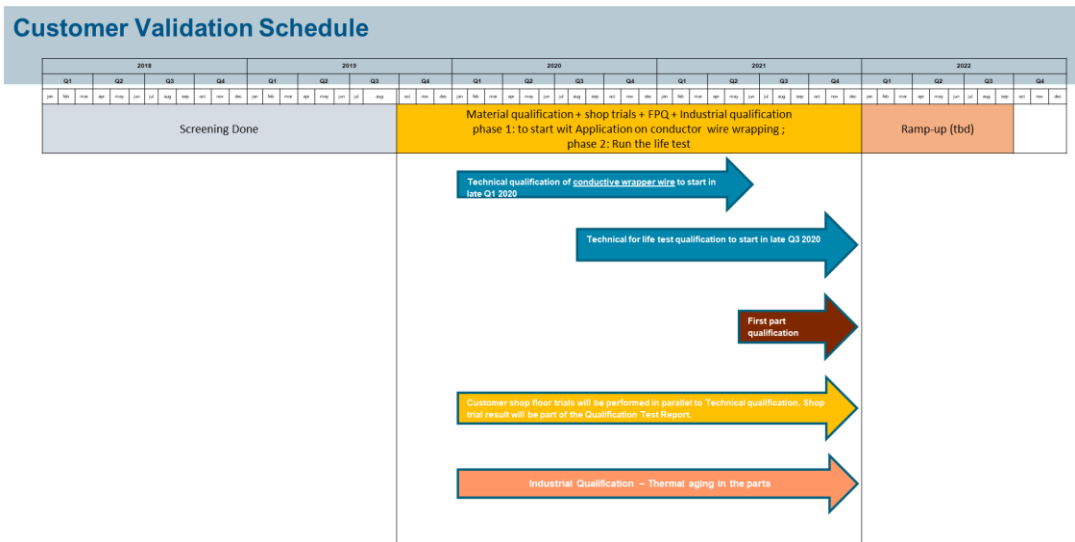
Figure 38: Voith Hydro meta-aramid conductive paper validation schedule.

CHAPTER V - CONCLUSION

5.1 Summary

The high impulse problem affects a number of different segments of the electrical industry, including the economic impact of downtime cost and the disruption to people's daily activities. The current solution is to use conductive or semi-conductor tape that is made by the combination of insulation materials of mica, polyester fleece and conductive material most commonly made of carbon particles. Carbon particles are easily released from the conductive mica tape or the conductive polyester fleece tape. They become contamination in an electrical insulation system that reduces heat transfer and leads to electrical tracking failure. The DuPont™ meta-aramid with carbon black is expensive and cannot be well adopted to the market place. The aim of this innovation is to provide a solution that combines conductive and insulating polymer materials, to develop a multifunctional system in which:

1. Polymeric materials provide the electrical insulating material
2. Polymeric materials provide the conductive material and absorb, re-direct and conduct high energy pulses safely out of the equipment

The Innovation Report focuses solely on the design, structure and materials that can be used as corona protection to absorb high energy impulses. The solution must be conductive and re-direct the high energy impulses as a corona protection material for the wrapping of the conductor wire in the form of a coil.

The structure of this Innovation Report started with introducing the significance of the problem and the current solution and challenges, then selecting the conductive and

insulation polymer, developing a new product specification and design, performing and executing the experiment plan, then finally reviewing the test results and deliverables. The experiment plan was developed to obtain sufficient data to extract suitable information to verify the hypothesis of integrating conductive polymer materials into insulation materials in order to develop a new conductive meta-aramid paper.   The data was gathered and analysed to qualify the processability and replicability of applying conductive polymer PEDOT: PSS in the process of meta-aramid paper making. The target physical and electrical properties were met by various prototypes which are made by different approaches or processes.

The specific experimental methods including the production process of making meta-aramid paper and the imitation for the meta-aramid paper production process in the laboratory have been implemented to qualify and test the hypothesis that the insulation materials of meta-aramid paper can be integrated with PEDOT:PSS in the processes of spinning (S2), fibrid fibridation (F2), paper making (B2, B3) and finally calendaring (C2, C3, C4) to achieve the target providing meta-aramid conductive paper for the wire wrapping application.

5.2 Discussion and Findings

The research findings include:

1. The integration of the conductive polymer of PEDOT:PSS into the meta-aramid production process,

2. The confirmation of the proportion of fiber and fibrid to meet the tensile strength,

3. The confirmation of the fibrid dimension and fibrid parameter of beating degree to meet the porosity (Submission II 6.1 & Submission III Section 3.2.4)

4. The confirmation of the most appropriate process of integrating PEDOT:PSS into meta-aramid making with coating process.

A simple and cost effective dipping process was applied. From the testing data collected in the experiment section (Chapter IV Section 4.5), the coated aramid material shows conductive behavior as the surface resistivity measurement is within 100 to 400 ohms/sq. The goal was achieved by B2 and also by finally forming the C2 final paper based upon the current data and findings. The target property performance is achieved with an appropriate concentration of PEDOT:PSS at 1% for the basic weight of 40 g/m2 for B2 (Table 15 & 16). The finding is that a percentage of less than 1% wt. PEDOT:PSS put on the meta-aramid materials will not have an effect on the construction of meta-aramid and meta-aramid fibrid as the mechanical strength of tensile strength has no particular changes. In addition, referring to the DSC scan of C1 and C2 in Section 4.5.8, there is no indication of decomposition at temperatures up to 300°C. B2 with additional (1, 2, 3, 4) layers of PEDOT:PSS can increase the conductivity (Table 17). The conductivity increases after calendering (Table 18). Thus, conductivity can be increased by various methods such as by increasing the PEDOT:PSS solid content or by increasing the coating thickness or layers. In addition, the conductive properties remained after the rinse water process. The thermal resistance of C2 is retained. Based upon (Figure 29) the C2's TGA data exhibits that across the entire test temperature range the pattern of weight loss of both C1 and C2 is similar (Section 4.5.9).

Table 27 summarises various types of specimens, process of integrating PEDOT:PSS and the result respectively:

Table 27: The summary of various types of specimens, process of integrating PEDOT:PSS and the result respectively

Process	Normal Specimen	PEDOT:PSS Specimen
Polymerization Process - Polymer Solution P1: Normal production polymerization process; P2: Add PEDOT:PSS solution to the P1 solution	P1	P2
Polymerization Process - Polymer Solution S1: Normal Spinning production Process by using P1 polymer solution; S2: coating S1 with PEDOT:PSS in the Lab (for further test purpose)	S1	S2
Fibridation - Fibrid F1: Normal Fibridation production Process by using P1 polymer solution; F2: forming fibrid film from P2 with PEDOT:PSS in lab (for observation)	F1	F2
Paper Making - Base Paper B1:Normal Paper Making production process by mixing S1 and F1 via paper machine; B2: coating B1 base paper with PEDOT:PSS in the lab; B3: Specimens of S2 mix with F1 forming B3 via the paper making machine	B1	S1+F1 = B2 S2+F1 = B3
Calendering - Final Paper C1: Normal calendering process; C2: Calendering process on B2; C3: Calendering Process on B3; C4: Coated PEDOT:PSS on C1	C1	C2 C3 C4

P2
1. PEDOT:PSS can be dissolved into the P1
2. After 24 hours, **P2** showed separation between two different polymers (P1 and PEDOT:PSS)

S2
1. S1 incorporated 1% PEDOT:PSS by coating method
2. **S2** has an average surface resistance at 106 ohms/sq.
3. **S2** after water rinse, surface resistance over the surface resistance measure limited
4. **S2** tensile strength remain the same
5. It is concluded that PEDOT:PSS cannot be integrated with S1 based upon the paper making process

F2
1. **F2** PEDOT:PSS were washed away during the water rinse process
2. It is concluded that PEDOT:PSS could not be integrated during the process of fibrid forming
3. The temperatures treatment from 100 °C to 300 °C had no significant impact

B2
1. Applying difference levels of PEDOT:PSS from 0.05%, 0.1%, 0.5% and 1% on B1 with basic weight of 22g and 40g, the surface resistivity of 22g and 40g B2 are similar per Table 15
2. The target property performance is achieved with appropriate concentration of PEDOT:PSS at 1% for the basic weight of 40 g/m^2 for B2
3. B2 with additional layers (1, 2, 3, 4) of PEDOT:PSS could increase the conductivity (Table 17)
4. B2 is success retain the PEDOT:PSS and meet the surface resistance requirement; thus, go to next step for calendering process

B3: The surface resistivity is 18,000 to 20,000; thus no further interest and experiments

C2
1. B2 with (1, 2 3,4) layers go for calendering process and become C2
2. The conductivity increase after calendering (Table 18)
3. The conductive properties remained after rinse water process

C3: The surface resistivity of B3 is 18,000 to 20,000; thus no calendering process is applied

C4
1. Using ink version of PEDOT:PSS for comparison purpose, obtain required conductivity and no significant impact on the base weight, tensile strength and the air permeability
2. The coatings were not able to be produced uniformly
3. Additive and resin contained in the ink version might affect the meta-aramid thermal resistance
4. Ink version is not preferred

P2: PEDOT:PSS can be dissolved into the P1. After 24 hours, P2 showed separation between two different polymers (P1 and PEDOT:PSS).

S2: S2 has an average surface resistance at 106 ohms/sq.; however after water rinse, surface resistance is increased to over 20,000 ohms/sq. It is concluded that PEDOT:PSS cannot be integrated with S1 based upon the paper making process

F2: PEDOT:PSS was washed away during the water rinse process. It is concluded that PEDOT:PSS could not be integrated during the process of fibrid forming. The temperature treatments from 100 °C to 300 °C had no significant impact on F2.

B2: Applying different levels of PEDOT:PSS from 0.05%, 0.1%, 0.5% and 1% on B1 with basic weight of 22g and 40g, the surface resistivity of 22g and 40g B2 are similar

(Table 15). The target property performance is achieved with appropriate concentration of PEDOT:PSS at 1% for the basic weight of 40 g/m2 for B2.   B2 with additional (1, 2, 3, 4) layers of PEDOT:PSS can increase the conductivity (Table 18).   B2 successfully retains the PEDOT:PSS and meets the surface resistance requirement; thus, B2 can go to calendering process.

B3: The surface resistivity is 18,000 to 20,000 ohms/sq.; thus of no further interest.

C2: B2 with (1, 2 3,4) layers goes to the calendering process and becomes C2.   The conductivity increase after calendering (Table 18). The conductive properties remained after rinse water process.

C4: Using the ink version of PEDOT:PSS for comparison purpose, required conductivity was obtained with no significant impact on the base weight, tensile strength and the air permeability.   The coatings were not able to be produced uniformly. Since the additive and resin contained in the ink version might affect the meta-aramid thermal resistance.   The ink version is not preferred.

In addition, several trials of larger scale production using dipping and gravure coating process were performed to seek an optimal, feasible production process and solution to multi-faceted production engineering problems and to obtain relevant information to set up future production processes and parameters (Section 4.8).   Optical examination for prototype meta-aramid paper and meta-aramid paper with PEDOT:PSS shows no substantial change on the structure of the paper (Figure 37).   Customers have provided a green light for screening in terms of meta-aramid conductive paper specification, physical properties and initial price to go for additional application verification for wrapping on conductor wire and life test for motor and transformers.   Altogether, an effective prototype gravure coating process of meta-aramid base paper with calendering

process afterward is presented to achieve functional conductive meta-aramid tape that offer a solution to corona protection applications in electrical insulation industry.

This research has evidenced that conductive polymer PEDOT:PSS can be integrated with meta-aramid paper production process after the meta-aramid base paper is made. With the calendering high temperature process, the meta-aramid fibrid undergoes a softening process which enables it to have excellent adhesion between the fibers and the PEDOT:PSS.   1% w.t. solid content of aqueous PEDOT:PSS has proved to enhance the meta-aramid conductivity to meet the target value of 100-400 ohms/sq. To increase the conductivity, either increase the solid content of PEDOT:PSS or increase the layer of coating.

5.3 Contribution of Work

5.3.1   The EngD Competency Contribution:

1. Managing the realization of a new product meta-aramid conductive tape from conception to the production trial, applying enhanced skills and knowledge from literature reviewed and project management such as stage gate to a new and unusual situation.
2. Development of innovation thinking and expert knowledge by putting insulation and conductive polymers in the paper making process, addressing a real industrial problem of aging issue caused by high voltage peaks.
3. Understanding the consequences in terms of practical applications of conductive tapes, industrial engineering in production process changes and new product development culture.

4. The ability to seek optimal, viable solutions to inefficiency of current conductive tape product performance/engineering problems and to search out relevant information by investigating the possibility of integrating PEDOT:PSS into five different paper making process.

5. Obtaining buy-in from all stakeholders internally from financial, production and purchasing personnel and externally from customers and PEDOT:PSS supplier and enriching oral and written communication skills while submitting submissions and innovation report.

6. Gaining management skill by delivering a project plan, utilizing stage gate management.

7. The author is able to apply the knowledge and expertise acquired in a business environment in a disciplined, innovative and penetrating way.

8. The methodology used in this research can be used to enhance meta-aramid paper function by adding another ingredient into meta-aramid paper.

5.3.2   *Academic Contribution*

1. Various studies of PEDOT:PSS coated on film, paper and polyester fabric have been examined in literature. The introduction of PEDOT:PSS to the meta-aramid process environment has not been previously reported. This research has confirmed and expanded the uses of PEDOT:PSS on meta-aramid paper in electrical motor and transformer industry.

2. The simple and cost effective coating process of the meta-aramid paper with PEDOT:PSS in this study offers low surface resistance achieved without significant impact on the paper structure so that the mechanical strength and thermal stability are retained.

3. Optimization of the process window for the PEDOT:PSS is needed for this program in order to achieve the target value of surface resistivity 100 to 400

ohms/sq. For commercial design it has been set at 1%wt., but the academic findings have shown it is effective at 0.7 % wt.

4. By understanding the process mechanism in greater detail, it was found that the conductivity can be adjusted by two different methods. These are either to increase the percentage of conductive polymer content or to add layers of conductive coating.

5.4 Commercial Value

The advantages of a meta-aramid product with a conductive polymer integrated can resolve the major problem of the carbon black conductive filler or metal pigment being worn off during the application processes.   Meta-aramid conductive papers are substitute products that can take advantage of overcoming the industry issue by replacing the current types of corona resistance materials.

Market Opportunity

1. New technology of flexible combined polymers of conductive polymer and electrical insulated polymer, together creates a new product that can resolve the problem of regular conductive wrapping tape where the carbon black is worn off into the insulation system;

2. While projections (See Submission IV 3.1) e.g. the transformer global market size is USD 1.6 million and the global market growth is around 6%, already show a significant market growth for the coming years, there are several scenarios showing even higher market growth and gain share than projected in the investment request;

Market Value

3. There are three meta-aramid makers in the world, that can produce meta-aramid paper from start at polymerization, spinning, paper making and calendering processes. None of them has provided conductive meta-aramid paper with using conductive polymer into the market place;

4. First mover - X-FIPER is the pioneer to utilize the two extremely different polymers conductive polymer and meta-aramid polymer to form a meta-aramid conductive product in the electrical insulation and high voltage, motor, generator and transformer industries;

5. It is unique conductive meta-aramid paper with high temperature resistance, flame retardant, tensile strength and conductivity;

6. Ability to support the move to a new technology via a whole insulation system (insulation materials with corona protection);

7. The development process and know-how means sufficient knowledge of the industry and existing appropriate customer contacts;

8. Current competitors are not yet providing this solution to the market place.

Price Advantages

9. The price is highly competitive as the comparative cost is lower. For example, the competitor selling price for the meta-aramid with carbon black is selling in the range of US$120/kg. Based upon the manufacturing and raw material cost, X-Fiper target selling price can be at least 30 to 50% lower;

10. X-Fiper is already currently selling our meta-aramid to the transformer and motor industry – thus it is cost effective to use the leverage with this conductive meta-aramid paper;

Future Opportunity

11. Beside the electrical industry, meta-aramid has been widely used for making honeycomb core in aerospace industry; for example, aircraft galleys, flooring, partitions, aircraft leading and trailing edges, missile wings and helicopter rotor blades. With the enhancement of conductivity with meta-aramid paper, this material could be developed for the applications that require an anti-static solution. Therefore, PEDOT:PSS could be integrated meta-aramid paper to increase thermal resistance and enhanced flammability resistance applying in the aerospace industry.

CHAPTER VI - FUTURE WORKS

6.1 Future work – Conductive Meta-aramid Paper

6.1.1   Thermal aging for high temperature

The key property for high temperature resistant electrical insulation or conductive materials is their continuous operating temperature. Meta-aramid paper can retain its electrical and mechanical properties while being exposed to temperatures above their continuous operating temperatures.   However, the high heat begins to degrade the insulation materials (Submission II Section 3.8.1). This degradation has the influence of reducing the tensile properties of the materials and ultimately destroying their integrity.   The meta-aramid paper has obtained thermal aging recognition of 200°C and above.   By integration with PEDOT:PSS, the thermal resistance or thermal aging capability is not affected (Section 4.5.8).   However, the conductivity was affected by the temperature increase.

Academic literature suggests that insulating hydroscopic PSS surrounding the conductive grains can swell or shrink considerably depending on humidity.   Besides, hydrogen bonds between HSO_3 groups of the PSS shells are broken as temperature increases, making the transport of carriers between the PEDOT:PSS grains more difficult. It was reported that heating PEDOT at 150°C (423 K) under ambient atmosphere causes irreversible changes in the polymer main chain to take place. Partial oxidation of the sulfur of the polymer backbone and the decomposition of the counter ion ($FeCl^-$) results in decrease of conductivity (Sakkopoulos *et al.,* 2014). However here, during the calendaring experimental process, the applied temperature is higher than 250 °C and increase in the conductivity was found (Section 4.5.5).   This

is different to that suggested by published research and may mean a case by case approved to application process is required. Additional work will therefore need to be done by the supplier to see how the thermal resistance of their product changes over a longer period of time. It should be noted that external validation and thermal aging tests for material of conductive meta-aramid paper still need to be carried out.

There have been several studies to show ways to improve the thermal aging properties. For example, the thermal aging capability can be improved by replacing helium for atmospheric air at 170°C for 30 minutes (Figure 39). More work needs to be done to ensure PEDOT:PSS can be thermally stable in application over a greater period of time.
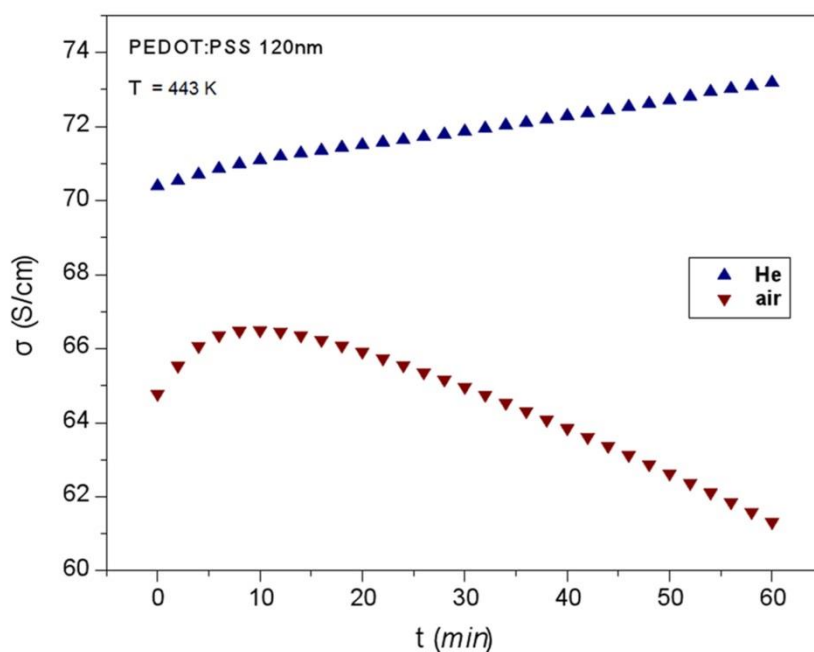

Figure 39: The changes of conductivity for the first heating of two PEDOT:PSS films, the one under insert helium, the other under atmospheric air at 443 K (170°C) for one hour (Sakkopoulos *et al.,* 2014).

6.1.2   Solution deposition – meta-aramid paper

In considering future production, uniformity of deposition or coating is a key to success in terms of thickness, uniformity and stability of the final product.   If the uniformity of the conductive meta-aramid paper is inferior, the electrical conductivity will vary within the paper; thus, the relaxation function of the electric field and antistatic capability may be inadequate.   There have been several studies related to the interaction of conductive polymer solution and substrate onto which it is applied.   One example is to modify the nature of the substrate (hydrophilic, hydrophobic) to control the distribution on the PEDOT:PSS. This method of "Pattern Chemical" has been well adopted in electronic device applications. (Brasjen 2012).   For future production run, further evaluation on solution deposition is required; for example, the study of using both line patterning and inkjet printing techniques for selective deposition of PEDOT:PSS on to flexible substrates could be evaluated as has been explored by Sankir 2008 (Sankir 2008).

6.1.3   Impact on the mechanical properties

For film applications, the strength of coating adhesion on the substrate and internal stress in the coating layers can result in shrinking of the coating, leading to brittleness in the coating layers or blisters from the substrate. Major influencing factors are internal stress, adhesive force and the elastic properties of the coating which will have an impact on the mechanical properties of the coating–substrate. (Wang *et al.,* 2013)   For a meta-aramid substrate, when compared to a film substrate, meta-aramid has a greater porosity property and therefore lower surface tension and thus, the conductive polymer such as PEDOT:PSS can be absorbed.   Experimental work here has shown that the tensile strength has not been affected. Furthermore, the ratio of the meta-aramid

substrate versus coating thickness is high; and the internal stress will not influence on the final product. For this product, the main application is for a conductor wrapping purpose, so bending will not occur. For verification, further study on the adhesive force and elastic properties can be carried out.

6.2 Other Potential Application – Conductor Wire

With regards to an electrically conducting part, magnet wire, triple insulated wire, or wrapped wires' conductor materials are usually copper. The problem of insulation destruction is directly related to the fact that electrical energy travels through copper at a speed of approximately 1/6th that of light in a vacuum. At this speed the placement of the high energy pulse which destroys the insulation is unpredictable. Therefore, if copper is to be substituted with conductive polymer, the high voltage pulse can be assumed to be reduced and absorbed. For conductive polymer to be substituted for copper as an electrical conductor, its conductivity and mechanical properties must increase. According to the literature review of current conductive polymers, with enhanced technology, both polypyrrole and polyaniline can be made as a form of nano-material that can act as an extrinsically conductive polymer when blended with thermoplastic or insulation polymer to increase its conductivity (Submission I Section 3.4.2). Thus, the opportunity is for conductor wire made by conductive polymer instead of copper.

6.3 Magnetically Conductive Polymers

Magnetically CPs could also be considered in combination with electrically conducting and insulating polymers.   To demonstrate the combination of magnetically CPs with the electrically conducting and insulating polymers (Figure 41), the approach can be designed to be as simple as possible. (Submission I, 3.6.2, 3.6.3)

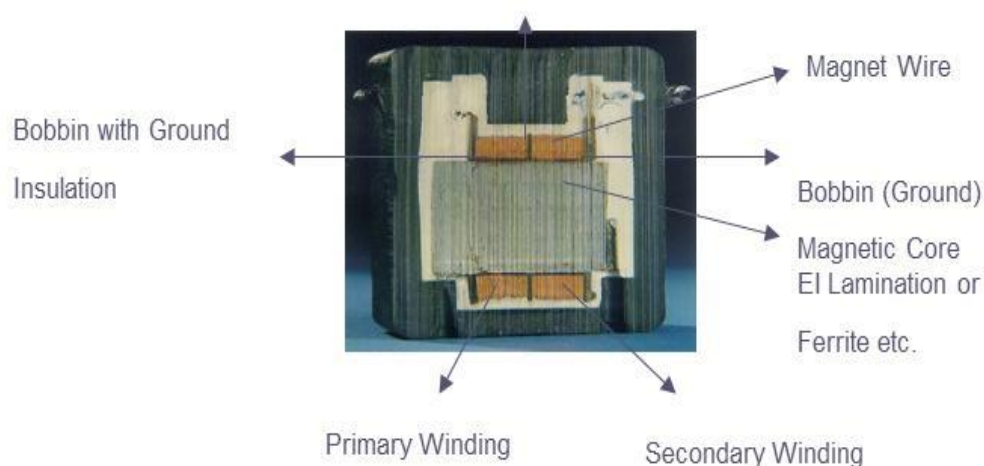Considering a transformer which includes a low voltage coil as an example:

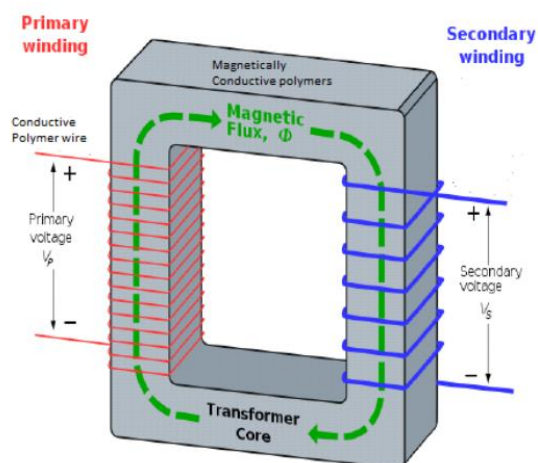Figure 40: Conventional Transformer Design (P,Leo & Co., Ltd training material 2017).

Figure 41: Idea of transformer coil made by conductive polymer wire and magnetically conductive polymer.

REFERENCES

Aldissi, M. (1992) Intrinsically conducting polymers: An emerging technology. *Series E: Applied Sciences* – Vol. 246, pp.45-50.

Amarasekera, J. (2005) Conductive plastics for electrical and electronic applications. *Reinforced Plastics* 49(8):38-41, DOI:10.1016/S0034-3617(05)70734-7.

Aramid. (2001, April 30). Retrieved November 12, 2012 from ttp://www.chem.uwec.edu/Chem405_s01/malenirf/project.html.

ASTM International. (n.d.) D646 Standard Test Method for Mass Per unit Area of Paper and Paperboard of Aramid paper. *Basis Weight.* ASTM International. Retrieved Jan 5, 2019 from https://www.astm.org/Standards/D646.htm.

ASTM International. (2004) D828 Standard Test Method for Tensile Properties of Paper and Paperboard Using Constant-Rate-of-Elongation Apparatus, Second Edition (#05106G)

Bahadoorsingh, S., Rowland, S. M. (2007). The Relationship Between Insulation Ageing and Power Network Performance. [Electronic Version] *IEEE Xplore* (DOI: 10.1109/ICSD.2007.4290782).

Bashir, T., Skrifvars, M., and Persson, N. (2017) High-strength electrically conductives: Functionalization of polyamide, aramid, and polyester s with PEDOT polymer. *Polymers for Advanced Technologies*, 29, 1, pp.310-318.

Brasjen, B. J. (2012) Coating and stability of thin liquid films on chemically pattern substrates. *Eindhoven: Technische Universiteit Eindhoven* D Ol: 10.6100/IR734478.

Choi, W. F., Cheng, E., Wong, P. (2006) Voltage and Pulse Endurance Test of New Generation wire CORONA-R TM developed by P. Leo – BC Wire ® 2006. Paper presented at *2006 2nd International on Power Electronics System and Applications*, Hong Kong, pp.40-43.

Christina, A.J., Salama, M.A., Rahmanb, Q.M., Wen, F., Ang, S.P., Voon, W. (2017, October 5) Causes of transformer failures and diagnostic methods – A review, *Renewable and Sustainable Energy Reviews*. Retrieved May 12, 2018 from https://www.researchgate.net/publication/318127474.

Cosnier, S., Karyakin, A. (2010) Electro-polymerization. Wiley, VCH, Weinheim, **p 215**

DuPont™ (n.d.). Electrical Insulation Materials – Nomex®. Retrieved Oct 21, 2015 from http://www.dupont.cn/products-and-services/electronic-electrical-materials/electrical-insulation/brands/nomex-electrical-insulation

Elantas. (2018). Retrieved December 15, 2018 from https://www.altana.com/divisions/elantas.html.

Elschner, A., Kirchmeyer, S., Lovenich, W., Merker, U., Reuter, K. (2011) PEDOT Principles and Applications of an Intrinsically Conductive Polymer, *CRC Press*, 2011 pp.9-10 123-124 & 168.

Feast, W. J. (1986). Synthesis of conducting polymers.   Handbook of Conducting Polymers, ed. New York: Marcel Dekker.

Friedberg, P. (2002). Four-Point Probe Manual. EECS 142 Microfabrication Technology. Retrieved November 10, 2018 from http://four-point-probes.com/four-point-probe-manual/.

Fujimori, Tatsushi, Naruse, Shinji. (2014, June 10). Conductive aramid paper and method for producing same.   Patent No.: US8747614B2.

Fundamentals of Conductive Polymers. (n.d.) *Material Matters Basic*, Vol 8, Aldrich Materials Science.

GB/T 451.2-2002 eqv ISO536:1995. Paper and Board – Determination of Grammage. National Standard of the Republic of China.

GB/T 451.3-2002 eqv ISO 534:1988. Paper and Board – Determination of Thickness. National Standard of the People's Republic of China.

Ghani, Supri A; Young, Heah Chong. (2010) Conductive Polymer Based on Polyaniline-Eggshell , Powder (PANI-ESP) Composites,   *Journal of Physical Science*, Vol. 21(2), 81–97.

Govindaiah, P., Kim, Y. D., Cheong, I. W. (2015) One-pot Synthesis of Grafted Brush Copolymers via a Chain-Growth Radical/Oxidative Dual Polymerization System. *RSC Advance*, Issue 114. Royal Society of Chemistry.

Hamzah, H.H., Saion, E., Kassim, A., Yahya, N., and Mahmud, E. (2007) Conjugated Conducting Polymers: *A Brief Overview*, JASA/ January 2007

Harun, M.H., Saion, E., Kassim, A., Yabya, N., Mabhmud, E. (2007) Conjugated Conducting Polymers: A Brief Overview. *Review Paper Jasa* 2, pp.63-68.

Herberts® - Electro Wire Enamels. (2000) Retrieved December 15, 2018, from http://www.performance-coatings.org/en/industrial-coatings/ct-he-pi-electro-wire-enamels.htm.

Hirai, et al., (2003) Enameled Wire. Patent No.: US 6906258.   Retrieved September 2, 2015 from https://patents.google.com/patent/US6906258.

Hokazono, M., Anno, H., and Toshima, N. (2014, June) Thermoelectric Properties and Thermal Staiblity of PEDOT:PSS Films on a Polyimide Substrate and Application in Flexible Energy Conversion *Devices. Journal of Electronic Materials*, Volume 43, Issue 6, pp. 2196-2201.

Immerman, G. (2018). The Real cost of Downtime in Manufacturing. Retrieved Feb 8, 2019, from https://www.machinemetrics.com/blog/the-real-cost-of-downtime-in-manufacturing.

Jagatheesan, K., Ramasamy, A., Das, A., and Basu, A. (2014). Electromagnetic shielding behaviour of conductive filler composites and conductive fabrics – A review. *Indian Journal of Fiber & Textile Research* Vol.39, pp. 329-342.

Judon, G., Beiec, M. (2005, April) Partial Discharge Signal Interpretation for Generator Diagnostics. [Electronic Version] *IEEE Transactions on Dielectrics and Electrical Insulation* (Vol. 12, No. 2) pp.297-319.

Kaur, Adhikari, Cass, Bown, and Gunatillake. (2015) Electrically conductive polymers and composites for biomedical applications. *The Royal Society of Chemistry*. https://doi.org/10.1039/C5RA01851J.

Lakshmanan, N., Rongasamy, L. (2008, September 9). Polymer Electrochromism on PEDOT coated fibers and Design of Electrochromic Pixel using Coated Fibers. *Examensarbete, Department of Physics, Chemistry and Biology, University of Linkopings.*

Lay, Mendez, Aguilar, Bun and Vilaseca. (2016) Strong and electrically conductive nanopaper from cellulose nanos and polypyrrole [Electronic version], *Carbonhydrate Polymers* 152 (2016), pp.361-369.

Le, T., Kim, Y., Yoon, H. (2017). Electrical and electrochemical Properties of Conducting Polymers. Polymer Review. Polymers 2017, 9, 150; doi:10.3390/polym9040150

MacDiarmid, A.G., and Epstein, A.J. (1991) Science and Technology of Conducting Polymers. *Technical Report* No.: NO.: 1991-12. P. 10-12

Material data sheet Nomex ® Aramid Paper Type 410. (n.d.) The Gund Company, Inc, St. Louis, Missouri ,USA.

Meta-Aramid Paper Testing Report. (2012). Electrical Materials Quality Supervision & Testing Center of Machinery Industry of China.

Mikhail, R., Levit, G. A. (2006). Electroconductive Aramid Paper, (U S) *Patten No*:US2006/0266486.

Morais, R.M., Klem, M.S., Ozorio, M. S., Gomes, T. C., Alves, N. (2018). Roughness Influence on the Sheet Resistance of the PEDOT:PSS Printed on Paper. *Current Applied Physics.* [Electronic version]. Vol 18, pp. 254-260, Elsevier Inc.

Murugan, A. V., Gopinath, C.S., Vijayamobanan, K. (2005). Electrochemical studies of poly (3,4-ethylenedioxythiophene) PEDOT/VS 2 nanocomposite as a cathode material for rechargeable lithium batteries. *Centre for Materials for Electronics* Technology (C-MET), Ministry of Communications and Information Technology, Government of India.

Naarmann, H. (2002) Polymers, Electrically Conducting. *Ullmann's Encyclopedia of Industrial Chemistry.* Retrieved Aug 20, 2016, from https://onlinelibrary.wiley.com/doi/abs/10.1002/14356007.a21_429.

Norden, B., Krutmeijer, E. (2000). Conductive polymers. *Advanced Information of the Nobel Prize in Chemistry*, p. 2.

Okamoto, Y., Pearce, E. (1985) Final Report: The Workshop on Conductive Polymers, Polymer Research Institute Polytechnic University, DE 87 006299.

Orgacon, (n.d.). Polymer from Orgacon® Electronic Materials. Advanced Coatings & Chemical Business group of Agfa Specialty Products.

P.Leo & Co., Ltd. Training Material

Parel, M.M.P., Gillado, A.V., Marvin U., Herrera, M.U. (2018) Morphology and electrical conductivity of polyaniline coating on acetate film. *Surfaces and Interfaces*, Volume 10, pp.74-77.

Penrose, H. W. (2000). Test Methods for Determining the Impact of Motor Condition on Motor Efficiency and Reliability. Retrieved September 21, 2018, from https://www.researchgate.net/publication/237543783_Test_Methods_for_Determining_the_Impact_of_Motor_Condition_on_Motor_Efficiency_and_Reliability.

Perkin, E. (2018) A beginner's Guide. Retrieved February 2, 2018 from https://www.perkinelmer.com/lab-solutions/resources/docs/faq_beginners-guide-to-thermogravimetric-analysis_009380c_01.pdf.

Pyrhonen, J., Jokinen, T., Hrabovcova, V. (2008) Design of Rotating Electrical Machines. *John Wiley & Son Ltd.,* P.455.

QB/T 1667 (1998) eqv. ISO 5636-1:1984. Paper and Board Air Permittiability. Industry Standard of the People's Republic of China

Ramakrishnan, S. (2011). Conducting Polymers: From a Laboratory Curiosity to the Market Place. *India Academy of Sciences*, pp. 1254-1265.

Rea Manget Wie Company Inc. Retrieved April 10, 2018 from https://www.reawire.com

Renmin, M. J. (2006, December 5) EU Directives and implications for the electronics sector. *University of China Asia Eco-Design Electronics Conference.*

Sakkopoulos, S., Vitoratos, E. (2014). Differentiation of the aging process of PEDOT:PSS films under inert helium and ambient atmosphere for two different rates of thermal treatment. *Open Journal of Organic Polymer Materials* (Vol.4 No.1), pp.1-5.

Sankir, D. (2008) Selective deposition of PEDOT/PSS on to flexible substrates and tailoring the electrical resistivity by post treatment. *Circuit World*, Vol. 34 Issue: 4, pp.32-37, Retrieve August 5, 2018 from https://doi.org/10.1108/03056120810918105.

Schmerling, Rolf, Jenau, Franl, Staubach Christian, Pohlmann, Fiedhelm (2012)   Investigations of modified nonlinear electrical materials for end corona protection in large rotating machines, *Conference paper.*

Schoch, K.F. (1983). Conductive Polymers: New Materials for Microelectronics.   *IEEE* CH1952-1/83/0000-0069.

Scott, J. C. (2010) History of Conductive Polymers, *John Wiley & Sons, Ltd.*

Shakweh, Y. (2018). Drive Types and Specifications. In Muhammad H. Rashid, (Fourth Edition), *Power Electronics Handbook.   Elsevier Inc.* [Electronic version]. pp.913-944.

Shirakawa, MacDiarmid, Chiang, and Heeger. (1977). Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene. *Chem Soc Chem Commun*, pp. 578–580.

Smela, E. (2003, March 17) Conjugated Polymer Actuators for Biomedical. *Advanced Materials*, 2003 15, No. 6.

Smith, W. (1999, September 21).   High Performance and High Temperature Resistance s – Emphasis on Protective Clothing. *Industrial Textile Associates.*, ITA, Greer, SC.

Soomor, I.A., Baharom, M.N.R. (2013, September). Comparison between partial discharge in paper and impregnated paper insulators used in power transformer winding based on ultra-high frequency

(UHF) detection method. [Electronic Version] *International Journal of Advances in Management, Technology's Engineering Sciences* ISSN:2249-7455 (Vol.11, Issue 12 (111)).

Stone, G.C., Boulter, E.A., Culbert, I., Dhirani, H. (2014). Electrical Insulation for Rotating Machines. *Wiley* P.21-23.

Stone, G.C., Culbert, I.M., Lloyd, B.A. (2007) Stator insulation problems associated with low voltage and medium voltage PWM drives. [Electronic Version] *IEEE Paper*, No. 1079-9931/07.

Supriya, P. (2009 November). High performance & their application. *Man-made Textiles in India*, pp. 379-384.

Suzhou Better Technology Co., Ltd. Retrieved Feb 20, 2018 from http://www.szbd2005.com/

Tadesse, M., Loghin, C.,Chen, Y.,Wang, L., Catalin, D., Nierstrasz, V. (2017).   Effect of Liquid Immersion of PEDOT:PSS-coated Polymer Fabric on Surface Resitance and Wettability.   *Smart Materials and Structures,* 26 005010.

Tendringpacific. Rapid Kothen Sheet Former.   Retrieved March 13 2017 from http://www.tendringpacific.com/instrument/rapid-kothen-sheet-former/.

Thorsen, O.V., Dalva, M., (2007, September). Methods of condition monitoring and fault diagnosis for induction motors. *European Transactions on Electrical Power*, DOI: 10.1002/etep.4450080510, pp383-395.

UL 746B Standard for Polymeric Materials – Long Term Property Evaluations, (1988).   UL Standard. Retrieved Sept 12, 2018 from https://standardscatalog.ul.com/standards/en/standard_746B

UL94 Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances, (1988). UL Standard. Retrieved October 22, 2013 from https://standardscatalog.ul.com/standards/en/standard_94_6.

Van Vooren, E. (2012) Type of Electrical insulation material, *EIU 104 Course*.

Voith Hydro. (2009, September) Micalastic® Insulation for high voltage hydro generators. *Technical data and illustrations*, t3346 e.

Von Roll (n.d.). Retrieved June 10, 2018 from https://www.vonroll.com/en/

Von Roll High Voltage Training Material, n.d.

Walkinshaw, JW. (2006). *Air resistance of paper (Gurley method – Revision of T 640 om-02),* TAPPI Testing Standard.

Wang, H., Guo, R., Shen, Y., Shao, Y., Fei, G., Zhu, K. (2019). Waterborne polyaniline-graft-alkyd for anticorrosion coating and comparison study with physical blend. *Progress in Organic Coatings*, 126 pp.187-195.

Wang, X., Grimoldi, A., Hakansson, K., Fall, A., Granberg, H., Mengistie, D., Edberg, J., Nilsson, D., Engquist, I., Berggren, M., Gustafsson, G. (2018).   Anisotropic Conductivity of Cellulose-PEDOT:PSS Composite Materials Studied with A Generic 3D Four-Point Probe Tool, *Organic Electronics,* ORGELE 5032.

Wang, X.S., Tang, H.P., Li, X.D., Hua, X. (2013) Investigations on the Mechanical Properties of Conducting Polymer Coating-Substrate Structures and Their Influencing Factors. Retrieved Jan 6, 2017 from http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2801994/

X-FIPER® New Material Co., Ltd. (2015) *X-FIPER® X-630 Material data-sheet*.

Yao, L., Zhao, W., Xu, S., & Sun, Q. (2013) The Preparation of aramid paper and its properties, *Advanced Materials Research* Vol. 796 (2013) pp.290-293.

Zhao X, Hirogaki K, Tabata I, Okubayashi S, Hori T. A new method of producing conductive aramid s using supercritical carbon dioxide. *Surf Coat Technol.* 2006;201(3-4):628-636.

ZXou, X; Liang J; Shao, Q; Sun, J; Tang, Z. (2013) Conductive aramid fiber with Ni-Cu composite coating prepared using the metalation swelling method.   *Polym.,* 14(3):453-458.