Feasibility study
on development of soft biosensors
based on conductive elastomers

Yu Han (MEng Biomedical Engineering candidate)

Supervisor: Youhong Tang

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Summary

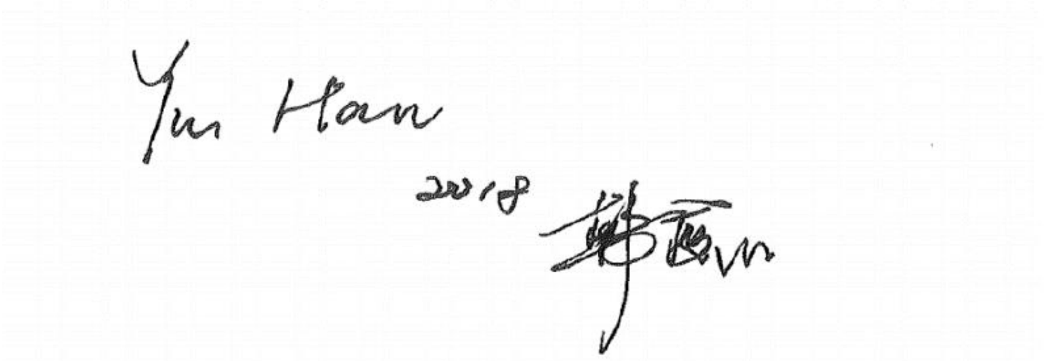
Quantifying naturally occurring strains in soft materials, such as those of the human body, requires strain gauges with equal or greater mechanical compliance. Strain gauges are devices designed to attach to a target object for the purpose of measuring deformations in a precise manner. The most common type of gauge consists of a patterned metal foil on a flexible plastic backing that attaches to the object with a suitable adhesive, such as cyanoacrylate. Deformations in the object lead to deformations in the foil, thereby cause its electrical resistance to change.

Electrically conductive rubber (ECR) is a promising class of material for this purpose, due to its intrinsically low modulus, low density, elastic mechanics and its pronounced piezo resistivity. ECRs can be prepared by dispersing conductive fillers such as graphene, carbon black (CB), carbon nanotubes (CNT) or metallic nanoparticles into elastomers such as poly (dimethyl siloxane) (PDMS). Moulding and curing processes can be used to manipulate such materials, which we refer to generally as conductive PDMS (CPDMS), into desired geometries for device integration. The electrical behaviours of CPDMS, such as the conductivity and the piezo resistance, depend strongly on filler concentration and morphology (e.g., particle size and structure) as well as filler-filler and filler-matrix interactions.

In this feasibility study, all-elastomer strain gauges have been fabricated with two types of conducting elastomer fibres made by CNT and PDMS integrated in a third, insulating elastomer to form arrays in the form of thin sheets. It can spontaneously and reversibly laminate onto human skin with the capability for quantifying and spatially distributions of strain. Particularly, when integrated with stretchable electronics and other classes of sensors, these technologies have the potential to expand the range of function that can be achieved in biointegrated systems, with potential utility in wound monitoring, human-machine interfaces and others.

Declaration

"I certify that this work does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text."



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Chapter 1. Introduction

In biological microelectromechanical system, there is no doubt that biosensor is one the most important branches. Besides that, most of the products and academic researches focus on high sensitivity biosensors for motion monitoring, vital sense monitoring and so on. One of the most popular biosensors is the soft biosensor, which maintain high flexibility, skin-conformity, and other outstanding properties. Meanwhile, the mechanisms applied on those biosensors are various, like electrical or thermal conductivity, mechanochronic, photosensitive, etc. One of the most popular mechanisms is electrical conductivity sensing mechanism, which is high sensitive, easy collecting, real time, etc. The electrical conductivity monitoring mechanism cannot detect the directions of the strain by single path. Most of the researches are focusing on circulating strain. These researches can indicate the proportional strain. If the strain sensors are capable for monitoring skin motions, the strain sensors should be able to sense the direction.

Meanwhile, most of conductivity sensing materials can only be tested in one direction of resistance or capacity gauge, which cannot apply for multi direction mechanical conditions. For example, some of the sensors which need to be able to monitor the strain change on the surface of human skin. Since multiple force affects the testing point, the single direction sensors are invalid to explain the real mechanical conditions. Therefore, the construction of sensing network is one of the solutions to sensing multiple directional force. For those strain sensors which need to attach on human body and collect useful data for monitoring strain change, it is a puzzle to satisfy the requirements as well. To complete this puzzle, the research needs to use STEM (Science, Technology, Engineering, and Mathematics) methods to design and evaluate.

Aim:

As for those reasons, a flexible, skin-conformity and attachable electrical conductive strain sensor with sensing network has been studied and the feasibility design and developing the sensor has been conducted in this research.

Structure of the thesis:

Chapter 2: Literature review of the thesis. Within this section, the paper introduced some former researches which were related to the topic. Furthermore, the part provided relative data to briefly indicate the mechanism chosen, conductive materials' application, scientific characterization, suitable fabricated method, and etc.

Chapter 3: Experiment part of the thesis. The research used precise procedures for fabricating & testing conductive elastomer to further strain sensors' fabricating. Then, the strain sensors' fabricating process was completed by using the results from former experiments. By using scientific methods, the fabricated strain sensor was characterized by stretching machine, digital multimeter, and etc.

Chapter 4: Result and discussion. The results for two types of strain sensors were mainly analysed form mechanical aspect, conductivity aspect, and practical aspect. To reveal the relationship between strain and direction, the research was using mathematic method to infer the internal association. Then, the research analysed the type I strain sensors' data of three angles' evaluation (0^o, 45^o, and 90^o) and one angle's test (random angle) to prove the system valid. Besides that, it also analysed the data of type II strain sensors' test (45^o and random angle). Furthermore, the research also provided the potential reasons for the final results. This segment has revealed the scope of the thesis. It has provided a framework for the whole process of this device fabricating, evaluating and testing. It offers an important contribution to the understanding of electrical conductive based multi-direction sensing strain sensors.

Chapter 5: Conclusion. This part gave a summary of total research. To be brief, the section came up with some major contribution of the thesis.

Chapter 6: Future work. This part was providing some suggestions for further exploration in this field by comparing others' researches. According to the comparison, future work needs to focus on conductivities' improvement, conductive network's construction, strain sensitivities' enhancement, and etc.

Chapter 2. Literature review

2.1. Biological Microelectromechanical system (MEMS)

After the second industrial revolution, recent decades have been witnessed the remarkable changes in our society. After the birth of the first transistor at Bell Telephone Laboratories in 1947, the 'microelectromechanical system' (MEMS) and relative micro size manufacture become more and more popular in recent society. More and more commercial applications are got familiar with the society, like pressure sensors. Within the recent years, technologies turn to more mature than before, including varieties fields, like engineering, physical science, biomedicine, and etc (Zhang 2017). MEMS is also playing a significant role in connecting the computer with our analogy system. Nevertheless, the 'biological microelectromechanical system' (BioMEMS) is a specific class of the MEMS, which combined the biological things with multiple measures and analyses of its activities, characterisations under any class of scientific study. The BioMEMS-based devices are an attractive field for microtechnology development. Due to the rapid development of the microtechnology, the accuracy and real-time detection are more and more important. For scientific analysis and detection system, virous outstanding detector and sensing mechanism in the BioMEMS and microfluid area are required, which has already been reported, such as microvalves, micropumps, micromixers, microchannels and microreactors for fluid detection. (Sang 2011)

Hence, a quiet lot of opportunities are shown in the related area of BioMEMS production, like the therapeutic intervention, fluid handling, bio-reactors, and etc. The BioMEMS world market got about 10 billion dollars in 2002, investigated by the European Nexus organization. The worldwide medical device industry business volume was about 2.17 billion dollars in 2006. By the increasing rates at 15% per year, the volume reached $4.97 billion by 2012, due to the analysis of Ernst & Young Pegs (Sang 2011). According to these figuration, the significant of BioMEMS market is obvious (Figure 1).

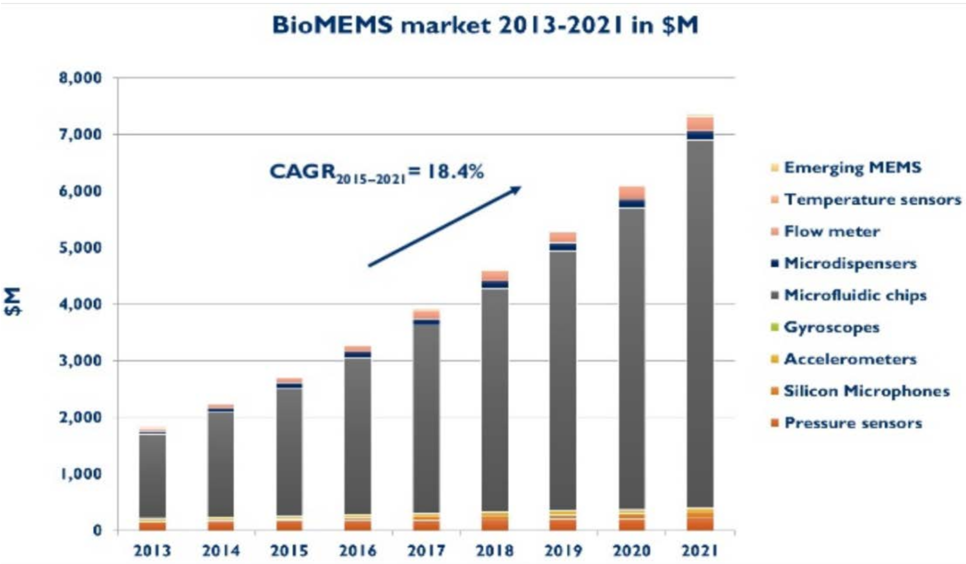

Figure 1. Global BioMEMS market size and forecast for some products (Scaringella 2018)

2.2. Biosensors and its affecting factors

Within the BioMEMS technology and products, the biosensors take the most important part in the process of information collecting with the technologically overhead development of the civilization. Due to the variety relative areas, the applications tend to be multiply choice, like genetics detection, disease diagnostics, drug delivery, environment healthy monitoring & industrial monitoring, quality control, security & threaten level evaluation, and etc.

To design a useful biosensor in a specific field by recent technology, multiplies factors need us to find a balanced state while testing, which might get the desired output. In general, there is one concept of biological sensors, which involve two major characteristics in addition to the combined signal processors used for the display of the results in an equally-system way: the sensitive biological element which is chemically receptive or selective layer, and the transducer or the detector element or sensing mechanism (which can work in variety ways) (Sang 2011). Moreover, there is a lot of other factors, which might affect the needed final result. For example, the temperature, moister hydration, the vapor of surrounding, etc. There is extensive amount of research in recent enthusiasm has been directed to wearable devices. Hight flexibility and wearable pressure sensors based on the mechanism, like piezoelectrical, electrical conductivity, mechanochromism and so on, are of deep impact for various applications, such as electrical skin, soft robot, and molecular probe (Zhang 2017).

In fact, most of the sensing technologies are faced with the issue of non-specific interaction. These side factors can make the sensing process messy, which make the sensing process complicated, the suitability of the sensor system for a special application, and false positive. Due to this factor, the output of fabricated devices is not matched with researchers' desired output. Generally, the devices will be designed to avoid these factors, or fixed by filter system. One of the choice is to maximize the sensor's sensitivity to the required response. The chemical reaction is one of the most sensitive methods to detect required signal. When the analyte recognized by the chemical layer, the transducer transforms the chemical simulation into required signal. The leakage of this mechanism is the elimination of physical transducer and chemical layer. If the system gets over this elimination, researchers will focus on both sensing layer and signal transducer. There is one of the solution, which do restrict the limit is the wearable devices. As for this design, the attachable device can sense the desired signal directly, and test several times to eliminate the side factors complicate (Sang 2011). The various concept for wearable biosensors has been introduced using the ultrathin substrates and highly flexible (pang 2015). Specifically, outstanding advances has been modified with non-invasive vital signal monitoring devices by ultrathin and ultralight layers with sensitivity matrix that can be adhered onto the surface skin. However, the body of human beings consists of many nonflat surfaces and fine topology, which is a challenge to contact on such irregular, us highly sensitive pressure sensors and integrate-multifunctional devices have been modified by using stretchable connection (Figure 2) (Pang 2015). Moreover, expect for its high performance and conformity of such devices, a suitable skin-attachable device that is simple to fabricate and robust for practical remote diagnose remains challenging to realize. In a nutshell, if it needs to apply the designed biosensor for sensing human body, the sensor will be flexible, high conformity, high skin attachable, etc.

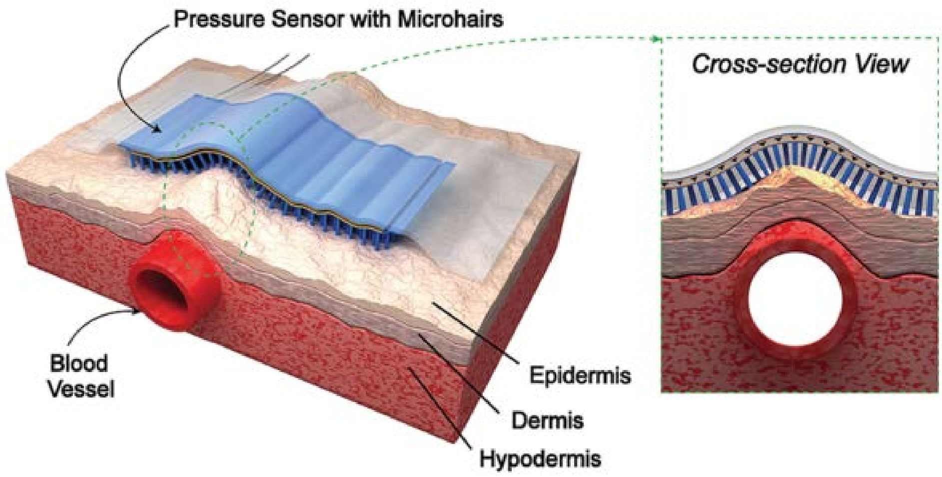

Figure 2. Highly skin-conformal microhairy pulse biosensor (Pang 2015)

Due to these factors and the experiences by predecessors, the soft biosensor is a desirable type for future human health research. Compared to the normal biosensor, soft biosensor maintains various supreme aspects, just as we mentioned above. Although soft sensors behave high performances, if we need to get desired output signal from human body, the research needs to find suitable sensing mechanism and sensing elements (Araby 2014).

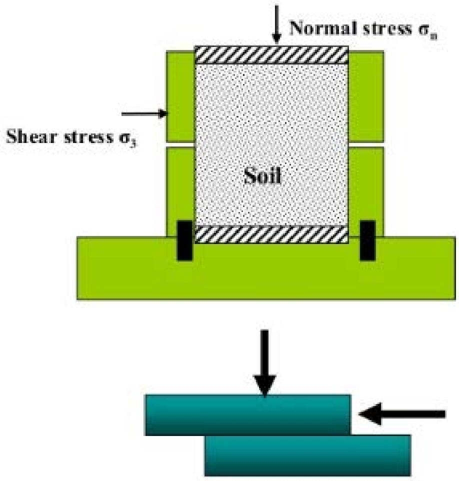

Figure 3. Shear test types (Araby 2014)

Furthermore, strain theory and mechanism are quite significant parts. Basically, shear stress for objects is hardly been tested directly through devices. Generally, there are two casual types of the regular shear tests. One of them, which requires that the sample be setup in a modified three points flexure or four points bend fixture. The main reason for generating this test is to load the sample so that the sample has two locations where the forces are applied or so that it experiences double shear. Each edge of the sample is anchoring. Meanwhile, the manual force is applied over the middle of the sample which tried to remove the midsection, so that both ends are left behind. Then, the second one requires that the sample have tapered ends that are each placed into grip fixtures that have been offset from the vertical axis of the sample. Then, the sample is pulled, so that the opposite faces are pulled in opposing directions (Figure 3). Due to these options, if strain sensor need to apply on body surface, the size and materials chosen needs to be suitable for reality situation (Araby 2014).

2.2.1. Sensing mechanism and examples

In general, there are multiple sensing principles that can applied on the biosensors: resistive and capacitive. These concepts have been frequency employed for providing tactile information by recognizing changes in electrical resistance and capacitance in response to external pressure in flexible sensors (Figure 4) (Woo 2014).

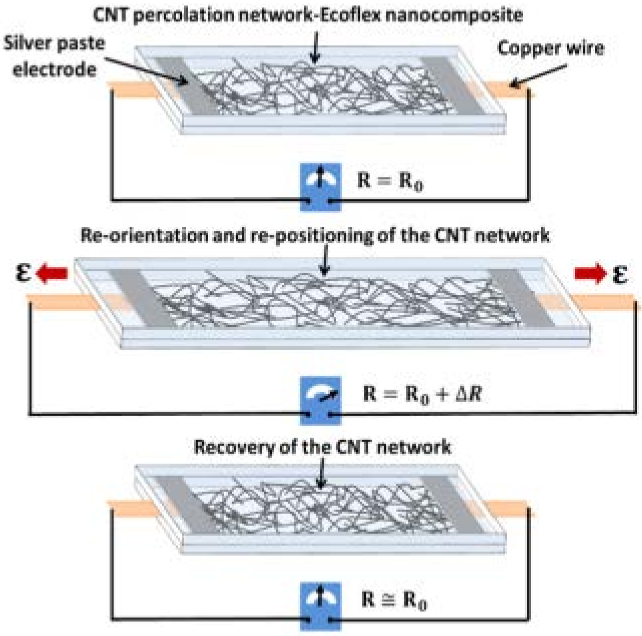

Figure 4. Electrical conductive mechanism

applied on CNT-Ecoflex nanocomposite strain sensor (Amjadi 2015)

As for this section, there is some other types high performances biosensors based on other mechanisms for sensing pressure or shear stress. Tee et.al based on piezo-resistive sensor to test flexible pressure. Their resistive based on the pressure sensors which relied on the conductive polymer composites materials that modulate the resistively by displacement of conductive filler in an elastic polymer. If apply any pressure on it, the inter-particles spacing between the conductive filler decrease, enhancing electron tunning and thereby lowering the effective resistance. If applied higher pressure, the conductive particles reach percolation. Moreover, the resistance decrease begins to reach an asymptotic value that depends on the intrinsic conductivity of the particles (Tee 2012). Furthermore, aspect from this mechanism, Amjadi (2015) and his team modified an artificial ultra-stretchable and skin-mountable strain biosensor by using carbon nanotubes-Ecoflex nanocomposites, electrical conductivity. The ultra-soft Ecodlex, which Young's modulus of 125KPa exhibits mechanical compliance as high as human skin as we needed. They supposed that strain sensors made by the CNT-Ecoflex materials, will be well-behave according to its strong interfacial bonding within the phases between nanocomposites. After their comparation of the aging effect with PDMS, Ecoflex is the suitable choice, based on its water resistivity, environmental-friendly, high stabilization, lower fatigue rates, and etc. Also, the biocompatible Ecoflex could be easily converted as skin-capable device by its high conformity & skin attachable. If the materials are being stretched from outside forces, the resistance within the nanocomposites will change due to this replacement, which transform the signal form strain verses force into electrical signal (Figure 5) (Amjadi 2015).

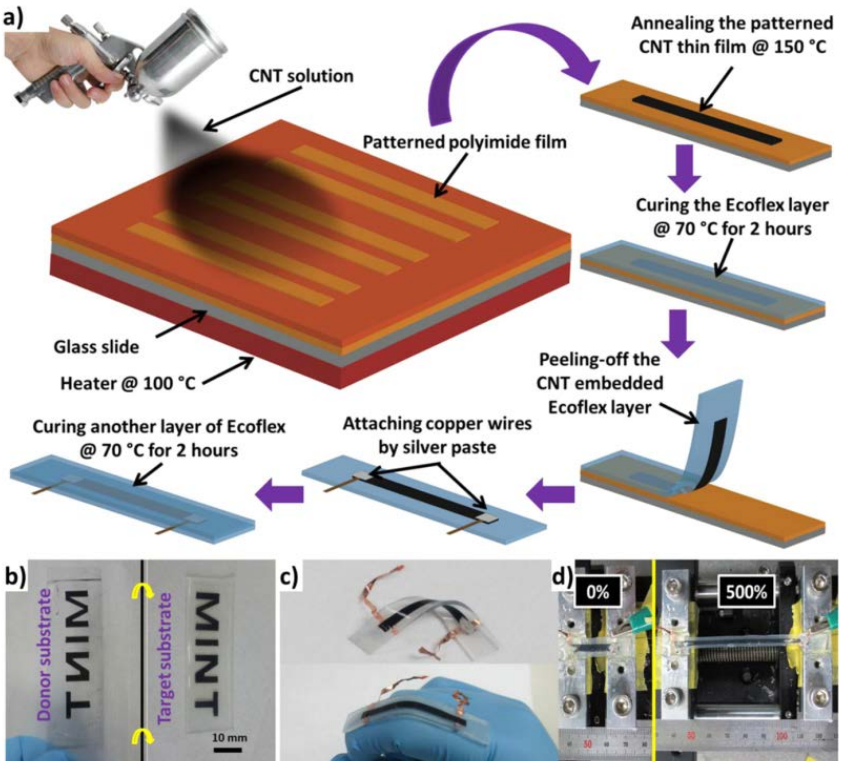

Figure 5. Fabrication of the CNT-Ecoflex nanocomposite-based strain sensor: (a) fabrication process. (b) photograph of the transferred CNT thin film with different pattern shape from donor substrate to the Ecoflex. (c) photograph of fabricated sandwich structured strain sensor when it is bent and twisted. (d) photograph of a strain sensor at the initial length and with 500% stretching (Amjadi 2015)

2.2.2. Sensing elements and examples

Besides the sensing mechanism, the other half part to proceed research is finding suitable sensing element. The sensitive elements of biosensor play a decisive role in the total biosystem. Furthermore, the basic for designing work is to design of the sensitive element, including the structural selection, the parameter optimization, and the materials selection (Sang 2011). Beam, cantilever and membrane are the main structures commonly used as the efficiency element of an indicator. Considered for about the structure chosen, the research has to find the suitable type in order to let system work efficiently.

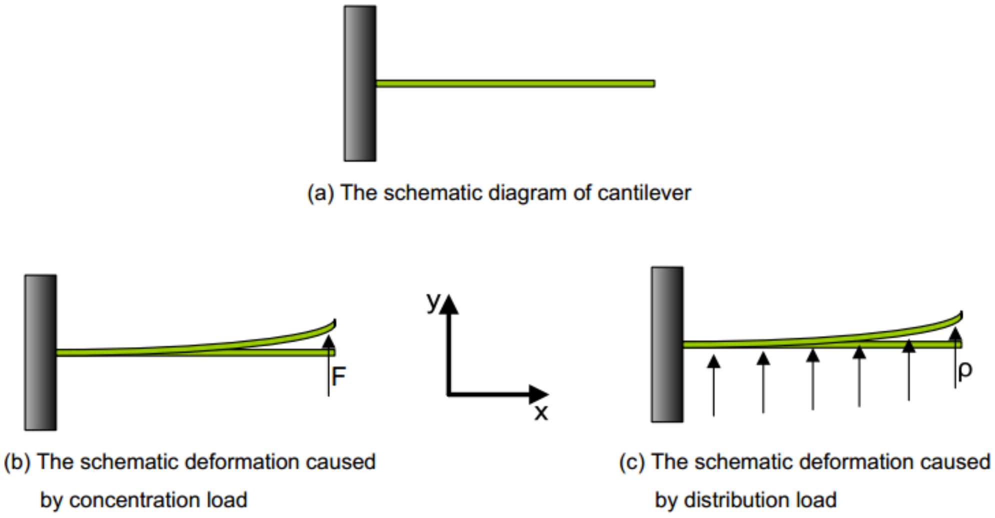

Figure 6. Sketch-map of cantilever structure (Sang 2011)

The typical cantilever is that on side is fixes, while other side is free (Figure 6). The load apply on the cantilever can be classified into two main categories: concentration & uniform. Several groups have done some researches and report in this area. They mainly focus on measurement of physical properties either by resonant frequency test or bending. Moreover, the physical properties which need to be considered within our design include temperature, pressure, power, Young's modulus, viscosity and density, current, frequency, and etc. Based on those variety factors, the surface stress sensors are a new class of this area, which maintain immense potential to satisfy the demand for better quality sensor. The 'surface stress' internationally represented by force per unit length (N/m), or by energy per area (J/m^2). Due to 'the forces are vectors, energy is scalar', sensing process need to isolate these elements. When testing reaction occur on the surface of such sensor, changes in intermolecular forces create a surface stress, which boost the curvatures on the mechanical sensing element. The range of surface stress in such reaction was reported to be 5 mJ/m^2 to 50 mJ/m^2, or reach 200 mJ/m^2, even 900 mJ/m^2 (Sang 2011). The sensing mechanism commonly used in cantilever-based biosensors are related to the changes in the deflection by induced variety surface stress, resonant frequency shifts by mass change, thermal change by bending, capacitance and resistance change by attachment of analyte on sensor surface or bending. Cantilever sensors will get a differential-induced surface stress rely on the adsorption of analyte, due to the varieties of top one and bottom one. The adsorption induced surface stress can be figure out by measuring the curvature of the cantilever bending with the 'Stoney's equation':

$$\frac{1}{R} = 6\left(\frac{1-\nu}{Et^2}\right)(\Delta\zeta_1 - \Delta\zeta_2) \qquad (2\text{-}1)$$

R is the radius of the curvature, t is the thickness, E is the Young's modulus, v is the Poisson ratio, $(\Delta\zeta_1 - \Delta\zeta_2)$ is the differential surface stress. For a L length cantilever sensor, which one side is fixed and the other is free, the tip deflection Δz can be calculated as followed:

$$\Delta z = 3L^2\left(\frac{1-\nu}{Et^2}\right)(\Delta\zeta_1 - \Delta\zeta_2) \qquad (2\text{-}2)$$

From recent research in fabrication of the sensing element, there are some research which maintain profound influences. Pang (2014) and his group demonstrated their portable sensor with a wireless transmitter, which is capable for sensing the weak signal stemming from the internal jugular venous pulses (JVPs). They use the microhair structure to sense the pressure signal from deep-lying vessel, which is very sensitive. This device transmits the pressure by the ending of the microhair structure through the thin membranes to the pyramid PDMS transducer connected with the Au/PEN electrode film, which deliver the mechanical signal into electrical signal. The materials for the microhair structure is PDMS, which improve the conformal contacts with skin (Pang 2014). Apparently, the structure for Pang's research involved various structure to improve the indicator sensitivity. Due the result they found, the combination is successful. Their micro hair structure, electrical membrane, and pyramid transmitter (Figure 7).

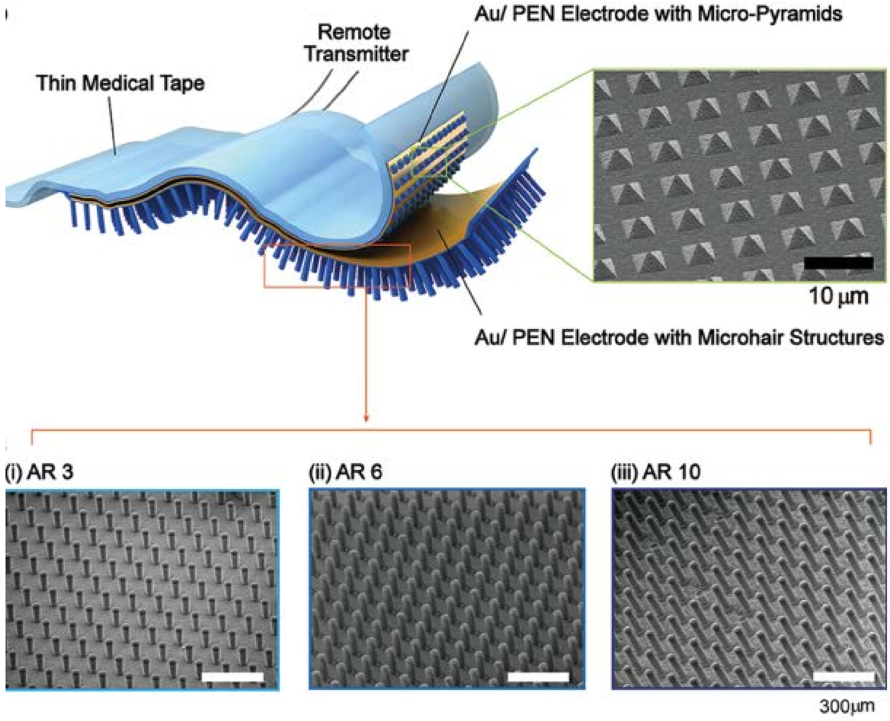

Figure 7. Cross-section diagram of microhair-structure sensor. The pyramid-shaped PDMS dielectric layer was placed between the two Au electrodes on PEN plastic substrates. (i) 3, (ii) 6, and (iii) 10 is the SEM images of dense microhair arrays with 30 μm radius and AR (Pang 2014)

2.3. Matrix materials chosen and design

As for the membrane, one intention within design process is to choose the best material to ultimate the sensor signal. Due to this concept, if researchers need to maximize the deflection for a given surface stress change, when the basic condition & parameter of the membranes are the same. Generally, PDMS, silicon nitride, PMMA, aluminium nitrides are the suitable choice for membrane materials. As known, a surface stress-based structure has two based layers: sub-material layer and contact.

Therefore, if the sensing system desires a satisfied outcome, the indictors would be better if it is a wearable device. This type sensor has attracted the world's attention due to the fascinating efficacy, and also maintain considerable progress along with the development of flexible and stretchable electrical sensors (Chen 2015). The reason for the popularity is due to their human-friendly wellbeing. The biosensor, which apply on human body need to be flexible, high biocompatibility, light weight, and etc. As for the wearable biosensor, it maintains flexible batteries, stretchable circuits, and flexible sensors (Shi 2016). For these devices, it can be easily attach either on human body or clothes, which can be utilized to indicate human signal of metabolism in medical industry. Especially, in health monitoring and rehabilitation assistance, wearable device can give us consist data for investigation. Furthermore, the wearable devices can be used as human-machine interface controllers. For example, it can provide us the data for human motion & emotion, as well as transforming the data into digital resource that can be used for further research. Also, it can provide us the entertainment control, like investigating immersive games and motion capture. The device can be used for sensing the desired signal to give us the key to find out the living organism mystery. On the contrary, the device can also act like a feedback collector, which can tell the differences between the outcome gesture and the designed output.

For this research, it will focus on fabricating soft biosensor for sensing shear stress. Due the measurement issues, the research will generate strain sensor to indicate the shear stress related to micro motions or macro motion. In order to fabricate suitable sensors, it should maintain following criteria: high durability, sensitivity and stretchability, and rapid response & recovery (Shi 2016). Due to these factors, the desirable sensor should be developed with high sensitivity and mechanical abilities. Because the sensor need to be satisfied with various appetite, like sensing sensitivity, durability, easy-access, and etc. All of these properties need to be suitable for human body, due to basic concept.

As our device designed for body use, the materials capability is accountable for our design. By this concept, the matrix materials chosen is quite significant. The materials should follow the rule of body application devices in the list of Therapy Goods Administration (TGA). As for the materials chosen, there are plenty of the materials can be selected in modern society. Generally, there are three types of the materials can be used: elastomer materials, ceramic materials, and metal. Basically, if the materials need to be adapted for body, the materials need to be soft and stretchable. Due to these requirement, the metal and ceramic materials will be little bit restricted by design properties. Generally, the elastomer materials are much suitable for high skin-attachable devices. Like the polystyrene (PS), polyvinyl alcohol (PVA), polycaprolactone (PCL), polydimethylsiloxane (PDMS), and etc (Fan 2013). Those materials can be fabricated by multiply methods to get the desired design. To screen out the basic condition of desired materials which will be applied to the desirable sensor, the following parts are going to operate a case study.

One of the most popular elastomers, called polydimethylsiloxane (PDMS). The PDMS in microelectromechanical systems (MEMS) technology is advanced, which provides new opportunities for huge amounts of biological and medical products (Mata 2005). The PDMS is a silicone elastomer, which could be cured with polysiloxane in relative level, with desirable properties that make it attractive for various research of MEMS and microfluidics components for biomedical applications. The adaption of PDMS for various field in Biosensor applications has been dramatically influenced by the development of Soft Lithography techniques, such as micro-contact printing, replica molding, micro-transfer molding, micro-molding in capillaries and solvent-assisted mirco-molding (Xia and Whitesides, 1998). Besides those, PDMS maintain other properties which is popular within academic research like transparent, non-fluorescent, biocompatible and nontoxic. And the PDMS has been traditionally used as a biomaterial in catheters, drainage tubing, insulation for pacemakers, membrane oxygenators, and ear and nose implants (Visser 1996). For the further exploration in biomaterial functional application of PDMS in combination with attractive aspects like low cost, mass-produced, microfabrication compatible, the polymeric basic biosensors make it formidable. Furthermore, the polymeric biosensor could promise the desired functional material for current and future BioMEMS applications. Therefore, it is a quiet significant interest in examining the compatibility of PDMS with both MEMS technology and biomedical applications (Mata 2005).

2.4. Electrical conductive filler chosen

One of the suitable sensing mechanism is electrical conductivity change related to sensing area, which means to transfer the motion change to electrical signal change. This idea is according to the sensing process, which need sensor to be much sensitive, light-weight, high accuracy, and etc. Within this area, the investigations have well cost-efficiency rate, as well as the outcome. In recent periods, more and more patent and papers are related to this area, and the application for these creations has bright future. Some of them used rigid materials, like metal thin foil or silicon, which has limited stretchability (max%<5%). A formidable challenge for researchers is combined high conductivity with various deformation. In order to fabricate flexible sensor, various conductivity materials have been investigated for this application. Such as carbon nanotube (CNT), carbon black (CB), CVD graphene, reduced graphene oxide (RGO), silver nanowires, and etc (Pang 2015).

2.4.1. Single wall carbon nanotubes (SWCNT)

Yamada (2011) and his team used the carbon nanotube film (Figure 8) to fabricate the sensor. They operated a single wall carbon nanotube (SWCNT) thin films which grown form patterned catalysts, using water-assist chemical vapour deposition. Single-walled carbon nanotube (SWCNT) thin films that transform its shape due to out force when stretched in a manner are similar to the structural deformation of a string cheese when peeled. Within this sensor, it can be measured and withstand strain-up to 280%, with durability (10,000 cycle at 150% strain), fast response (delay time,14ms) and low creep (3.0% at 100% strain). To make long films of arbitrary length, films were individually removed and laid with a 1 mm overlap side by side, on a flat elastomeric dog-bone-shaped substrate (Yamada 2011).

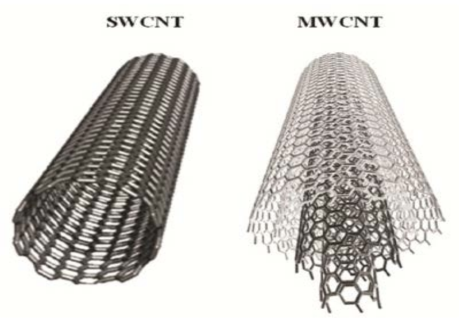

Figure 8. Two types of the CNT (Yamada 2011)

2.4.2. Graphene platelets (GnPs)

shi (2016) and their team used the expandable graphite to fabricate the worm-like graphene platelets (GnPs) (Figure 9), which embedded on the polyethylene terephthalate (PET) materials scaffold, covered with polydimethylsiloxane (PDMS). After prepared these layers, they used the force devices to make them adhere to the attachment on medical tape. Furthermore, the scaffold designed by auto computer-aid-design can be various due to their applications. Within their fabrication, the methods they applied are well behave in cost-efficiency, structural integrity, oxidation prevention, and higher quality for sensors. Due to their fabrication, the conductor sensor part exhibits an excellent recovery rate with medical durability through 550 stretching cycle, which is much superior than its peer graphene film fabricated by pencil drawn. And their row materials for this composite like medical tape, expandable graphite, polyethylene terephthalate (PET), and polydimethylsiloxane (PDMS) are easy-access, as well as its prices. Their sensor can work by translating minor micro-structural deformation into precise electrical signals. As for fabricating the transistor, they put the expandable graphite in a crucible at around 700 centigrade for 1 minute. The thermal expansion transforms the compound into worm-like graphene platelets. The thermal gasoline squeezes the 2-diversional graphene films, which will be isolated to each other. Due to these methods, the chemical waste will be much smaller than normal methods.

Figure 9. Expanded graphene nanoplate (GnPs) (Shi 2016)

2.4.3. Hyper phase conductive fibers

Besides those, there are some other fabricated materials used for conductivity devices. For example, the extruded reaction conductivity fibers. Allen (2014) and his team used the single-walled nanotube (SWNT) powder as the basic conductivity mediator, combined with some assistant materials to make the conductivity fibers (Figure 10). The assistant ingredients are regioregular poly (3-hexyl thiophene) (P3HT) and 3,4-ethylenedioxythiophene (EDOT). These two elements are important for single wall nanotube (SWNT) to be align and dispersed. They put these materials into 1,2-dichlorobenzene (oDCB) to make a dispersion of single-walled nanotube (SWNT). The solution was then sonicated by Cole-palmer Ultrasonicator at 300W for 15 min into ice bath. After the sonication, the material will be dispersed into the solution, which looks like low yield stress gel. Then the fibers will be formed by flowing the ethanol solution with single-walled nanotube/ poly (3-hexyl thiophene/ pyrrole dispersion in 1,2-dichlorobenzene (oDCB) using a syringe pump and a peristaltic pump. They use the average velocity of 15 mm/s to squeeze out the dispersion. Meanwhile the ethanol solution velocity should around 65 mm/s. The conductivity fibers collected by this method, has a conductivity of about 6 and 7 S/cm for SWNT/P3HT/PPy. The diameter of these fibers is about 70µm, which wrinkles within it that seem to consist of nanofibers of about 30 nm in diameter as seen.

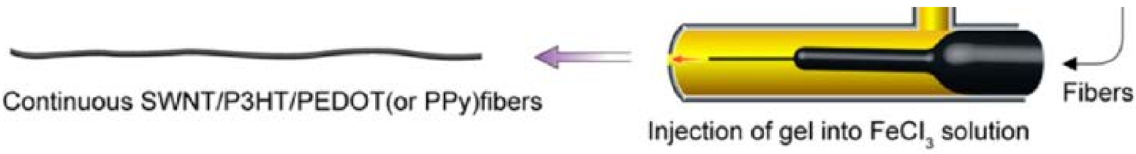

Figure 10. Nanofiber (SWNT/P3HT/PPy) injection (Allen 2014)

2.4.4. Graphene

Graphene materials are sensitive, which is also one of the easy access. There are several methods to collect this kind of material. Fortunately, most of them will collect wellbeing graphene powder or dispersion. The graphene is compromised with tightening stacking carbon atoms, which will be shape in the 2-diversion honeycomb. Due to its unique 2-diversion crystallization structure, the graphene materials maintain excellent mechanical properties, electronical properties, thermal properties, and magnetism properties. The graphene fracture strain of ca.25%, and its Young's modulus of ca.1TPa. Furthermore, it also has good optical transmittance, which overcome the limit performance of traditional transparent electrode materials. It maintains superior electrical properties, such as high carrier mobility, and well piezoresistive sensitivity (Houk 2016). All these properties are basic on graphene's microstructure, which maintain lot of π bonds within the gap between each two slices. Due this factor, the composites materials maintain graphene, could maintain significant properties by π-πfunctional combination. Due to this concept, conductivity materials can be strength by this property (Fan 2013). As for the hydrogen bond and π-πfunctional combination, these functional bonds generally will be function with hydroxyl, carboxylic acid/ or epoxy functional group, which affects the original molecular structure integrity of graphene oxide (GO) or reduced graphene oxide (RGO) composite system. In reality, the graphene sheets are hardly being dispersed into uniform sheet (Figure 11). Therefore, the applications of graphene materials are restricted by this property.

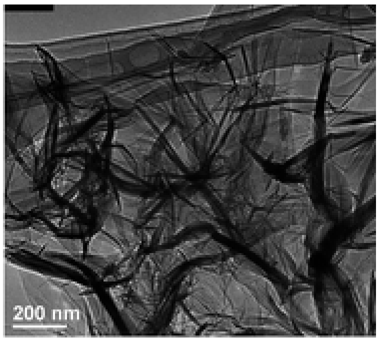

Figure 11. TEM image of graphene sheets by 200nm (Fan 2013)

According to those introduction of these conductive materials, the research chose graphene and carbon nanotube combined with realistic experiment conditions.

2.5. Fabrication design

To get desired testing materials, the fabrication is the major part of the design. generally, there are lot of researchers who keep working on this project, which give us much formal experience in this field. The researchers' choices are generally focus on the energy chosen and the application place. There are multiple choices for fabricating the design, which include easy access one and hard one. The easy access energy systems for fabrication tend to be simple, like heating method. Meanwhile, the hard access energy systems tend to complicate, like chemical method. Furthermore, the mechanical structure of the strain sensor needs to be sensitive enough to collect the strain change on the surface of the skin. Compared to the recent strain sensor in conventional sensor, mainly focus on the conductivity change among one direction rather than multi direction. Due to the geographical appearance of the surface skin, single direction strain sensor cannot satisfy the recent academic requirement. Therefore, the strain sensor need to construct a network, which could efficiently test (Lou 2017). Lou and his team fabricated a kind of ultrasensitive and ultraflexible e-skin with dual functionalities for wearable electronics (Figure 12). Due to their concept and work, the conductive network can sensitive enough to detect micro changing from the air. Therefore, their prototype can be used for sensing the air flowing change while speaking, which is a mazing work. They are using the Au electrode, ultrathin PDMS, Multi wall carbon nanotube, PANI hollow nanospheres to fabricate this strain sensor.

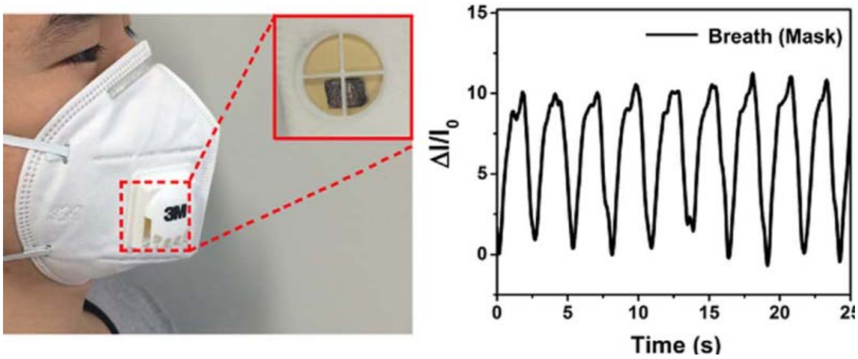

Figure 12. Ultra-flexible e-skin fabricated by Lou's team (picture is for testing the breathing caused length change)

2.6. Side factors of sensor design

To satisfy the requirements' output, side factors within this system is also the essential part among the process. The environmental requirements of biosensors defined its application and working situation. The major environmental requirements include the temperature, the physiochemical properties of the medium, substrate materials, and the dissolve gas mixture to be adequate. These factors, which mentioned above must be considered for the design of biosensors (Araby 2013).

For some of biosensors, its analytes need to contact with the interface of the substrate directly to detect the desired signal. Within this process, the analytes system must attach to the researched object in order to react. In some cases, thin films have been shown to support device adhesion and growth, like PDMS, silicon nitride, silicon carbide, and etc. As for the temperature factors, most of the biosensor is used for human body, which should be worked around 37°C. It is quite significant to keep the constant temperature or regulate the temperature of the biosensor to keep devices into high-performance state. As for the gas phase issue, there are two major constituents of the gas phase for constant condition: oxygen and carbon dioxide. Oxygen is the main component in metabolism. The consumption rate of human cell is approximately 20 amol/cell/sec to 100 amol/cell/sec (Sang 2011). Carbon dioxides are not only the waste of regular cells' metabolism but also required for most cell types to maintain the pH through the bicarbonate buffer system. If oxygen tensions above approximately 35 kPa (varies by cell type), the inhibition of cell growth and cellular degeneration can occur after 48 hours of exposure. Moreover, the cytotoxicity part is one of the most significant part in designing biosensors. The cytotoxic materials leach physiologically important amount of toxin over the duration of the sensors' lifetime. Generally, the materials used in biosensor modification cannot dissolve in connecting media nor leach more quantity. Otherwise, the toxin of these materials will generate some side effect on the growth rate, metabolism, or viability of the cell or skin (Sang 2011).

2.7. Micro phase mechanism of strain sensor

To fabricate a suitable strain sensor, the research applies those filler materials into matrix. Therefore, because of the fillers' various aspects of function, all types of the strain sensors behave in multiple ways. To well learn the sensing mechanism of the strain sensor, the research need to study the microstructure and micromotion. Then, the fabricated strain sensor can be predictable and reliable. For those conductive filler mentioned above, the most suitable choices for strain sensor can be graphene, carbon nanotube (CNT), metal particles and etc. Due to fabricating processes and practical operation, the research mainly focus on graphene and

Multiwall carbon nanotube (MWCNT). According to the former research mention (Lin 2013), the strain change and electrical conductivity change relationship can be described into the interaction of conductive tunnelling micromotion. Within the fabricating process, the conductive particles as fillers added into the polymer matrix. If the system wanted to maintain conductivities, the conductive tunnelling connection needs to be consistency and coherency. Due to the external stretching, the conductive tunnel stretching by the internal shape change. Within 10% strain stretching ratio, the conductive tunnel slightly changes. If increased the stretching ratio to 100%, the conductive tunnel starts to lose part of the connection with nearby conductive junction (Figure 13).

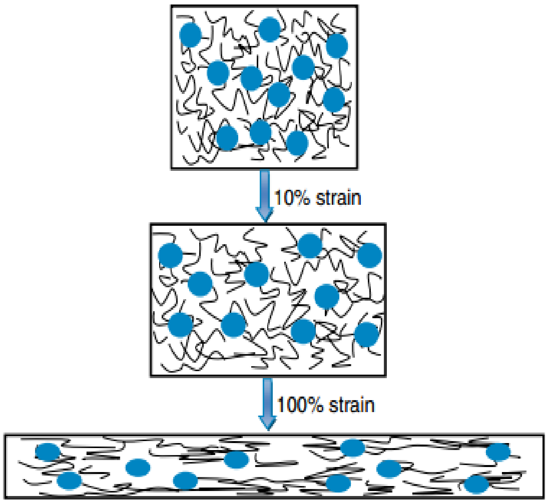

Figure 13. Schematic of conductive networking during the stretching process: top, without strain; middle, 10% strain; bottom, 100% strain (Lin 2013)

The dots represent the conductive metal particles fillers concentration point and the curve represent the carbon nanotubes (Figure 13). Apparently, the internal shape changes applied onto the strain sensor leads to micro separation between nearby conductive particle. Therefore, the conductivity properties reduced within this process, which can use for sensing the strain change. Due to their SEM (scanning electron microscope) images, it proved the diagram estimation, which indicated the micro mechanism (Figure 14).

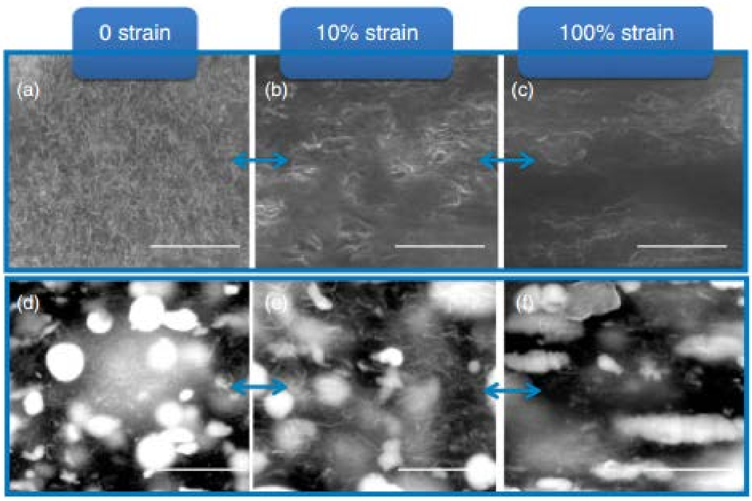

Figure 13. SEM image of the CNT & metal particles filler stretching test (Lin 2013)

As Figure 14 shown, the CNT filler was being stretched by the shape change. With the increase of the strain change, the conductive filler tends to lose interaction with each other. Therefore, the conductivities reduce can be explain by the micro structure change (Figure 14).

Due to this research aim and requirements, the strain sensor need to improve the stability and skin conformity while sensing. Therefore, the mechanical properties of the strain sensor need to be flexible enough to capable for human skin. Besides those, the fabricating process need to be clear and simple. If the strain sensor wants to be sales into the market, the fabrication cost for single strain sensor reduced to a relative low price. Therefore, the conductive fillers' treatment need to be simple and efficiency.

Chapter 3. Experiment

3.1. Preparation and materials

To fabricate conductive rubber and high flexibility sensors, the silicone rubber (polydimethylsiloxane, PDMS) can meet the desired output. A room temperature vulcanizing two parts silicone rubber: Part A and Part B (RTV-2 SR, Barnes Products Pty. Ltd., Australia) used as matrix. Part A is polysiloxane with some function al group. Part B is polydimethylsiloxane with some functional group.

As for the conductive materials, carbon nanotubes (CNT) and graphene had been used for conductive functions. Carbon nanotubes materials were chosen: Multiwall carbon nanotubes (CNT) (MWCNT, degree of purity >97%, diameter10-20 nm, length <2 um, ash <3%, special surface area 100-160 m^2/g, Shenzhen Nanotechnologies port Co. Ltd., China). Graphene materials were chosen: Graphene NMP suspension (SE4101, solid content 4.0±0.1%, thickness <10 nm, impurity metal content (take Mn and Zn meters) <5.0 ppm). In order to get better dispersion of graphene, the manufacturers use the NMP (N-methyl-2-pyrrolidone) to disperse (well dispersed graphene sheets maintain supreme function).

Therefore, for a uniform dispersion, master batches of the rubber contain 4.0% carbon nanotube (CNT) & 3.0% of graphene (all the relative conductive rubbers are made by ourselves). In order to get accurate conductive properties, the research also finished the testing of the series samples of 4.3%, 3.5%, 3.0% CNT conductive rubber. The strain sensor based on those results and fabricate as followed.

3.2. Fabrication of the conductive rubber samples

The fabrication processes are indicated into section. For further experiment set-up information, it will be found in Appendix section (Figure A1-A6).

Figure 15 shows the fabrication process of the Multiwall carbon nanotube (MWCNT) conductive rubber. Due to the solid phase of CNT, in order to get better dispersion within the rubber, ultrasonication bath and homogenization machine need to be used within the fabrication. Furthermore, to avoid uneven mixing, the CNT powder needs to be added into part A and part B individually. While adding the CNT powder into both parts, the mixture viscosity is too high to be mixed uniformly. During the process, the aceton is one of the additional solutions to help mixing. Therefore, the aceton needs to evaporate within this process. Within the ultrasonic process (200 watts and 42 kHz, the temperature should be controlled within 10°C by freezer), the container of the mixture should be covered with plastic wrap to avoid other impurities into the system. To vapour out the additional aceton solution, each part of the mixture need to be treated within the vacuum oven. Each of them was treated in the oven for 60°C, 760 mm Hg, 24h. After vaporing out, the research weighted the system and compared with the former system. Then, the mixture needs to be analysed by using scientific calculation, to monitor the system with additional solution or other impurities. After cooling down, the mixture can be mixed together to fabricate desired conductive rubber. Cured samples need to be set at the size of 25mm × 25mm × 3mm. This process is only for the fabrication of Multiwall carbon nanotube conductive rubbers.

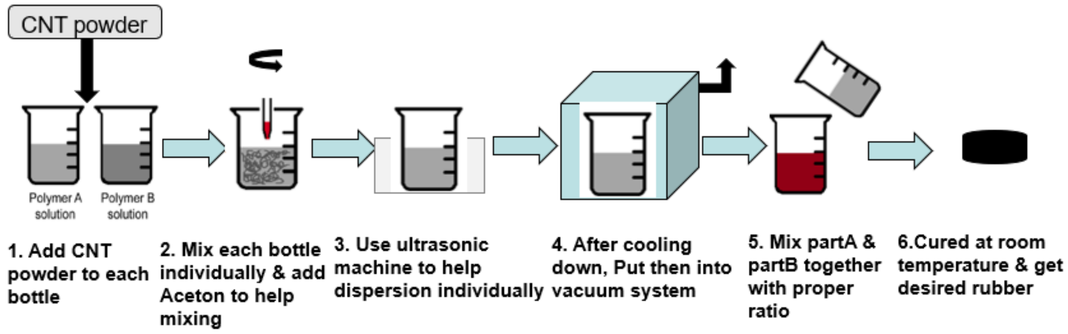

Figure 15. Diagram of the CNT conductive rubber fabrication process

The graphene conductive rubber fabrication needs further treatment (Figure 16). By using graphene NMP suspension to fabricate conductive rubber, one of the biggest issues is the solution NMP (N-methyl-2-pyrrolidone), which has a stable, high boiling point, high solubility in many organic material, low volatile. To avoid destroying the functional group of part A which acts as crosslinker, graphene NMP suspension needs to be added into part B individually. Using the magnetic stirring machine to mix the part B & graphene suspension, the rotating speed is 600 rmp at room temperature. As for the vapouring system, it should be worked into the fume hood. Before the vapouring process, the mixture should be weighted to get the exact value of the NMP solution. The vaporing gas needs to be collected rather than leave it (Irritant gas to skin & eyes). After the vapouring process, the mixture should be weighted again. Then its weight loss can indicate the solution condition of NMP content. After repeated this weighting and vapouring process, the mixture can be used for the curing process. If the curing process cannot complete, it might be the problem of NMP remaining.

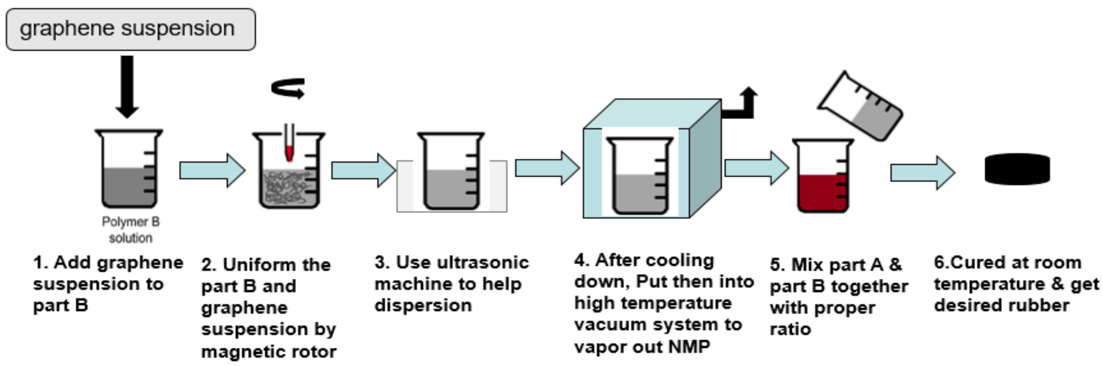

Figure 16, Diagram of graphene conductive rubber fabrication process

3.3 Fabrication of the sensor samples

Apart from the conductive rubber fabrication process, the sensor fabricating procedures will be much easier. The fabricating processes mainly focus on the sensors' flexibility, conformity, high skin-attachability. In order to get the desired network, two slices of conductive rubber layers are compulsory. To meet these requirements, 3.5% CNT conductive rubber and 4.0% CNT conductive rubber are chosen. The reason for choosing these two types is based on the fabricating process, electrical conductivity properties, and mechanical properties. Compared to these two types, 4.3% CNT conductive rubber has less mechanical performance, similar conductivity properties with 4.0% one, and complicated fabricating process. As for 3.0% graphene conductive rubber, although it has outstanding conductive properties, less mechanical performances and complicated fabricating process made it rank last in this competition. Put one of these two types of conductive rubber on the surface of the slides. Cover this conductive rubber with a slice of 0.5mm thick normal banana skin rubber (this process will avoid two conductive rubber having direct connection, no overlap). Put the other layer of these two conductive rubbers layer on the surface of the thin normal rubber film. Pour the normal uncured rubber on this junction slowly & distribute well. Make sure that there will be no air bubbles within the whole process. Then, slowly put another slide onto the surface of the normal rubber & conductive rubber junction. Put these 'sandwich' like samples into the oven for 60°C, 1-3 hours. Take out and cool down to room temperature. Furthermore, to guarantee the shape of the sensors' samples, there will be two wooden stick on the both end of the rubber to keep it in desired regions (wooden stick: D=1mm, length relative equal to 25mm). The size of the strain sensor samples need to be controlled within 25mm × 25mm × 3mm, which overall weight needs to around similar figure. In order to improve the sensitivities, this research also designed a series of experiment with similar conductive rubbers by putting two slices of 4.0% conductive rubber into the strain sensor.

All the relative products fabricated within this research is made by ourselves (Figure 17). The strain sensor samples are the prototypes that tested within this research. The main concept for designing this prototype is to test various directions of external stretching. In order to tell the differences between the monitoring processes, strain sensors have been designed with two different conductive rubbers connecting networks.

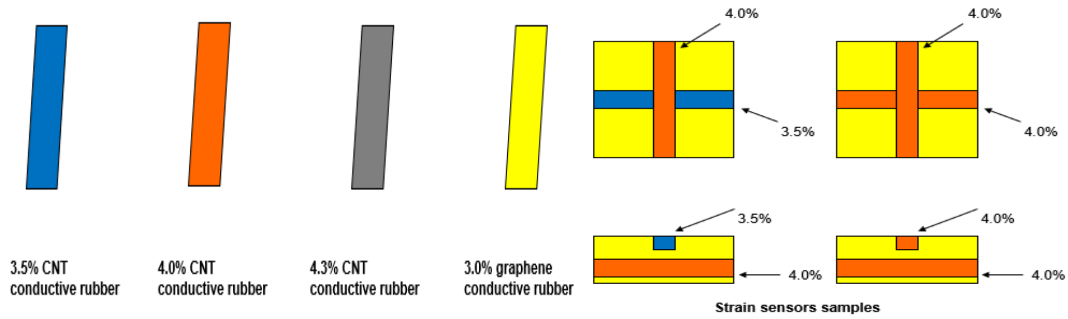

Figure 17. fabricating products and strain sensor samples

(Distinction colours of these conductive rubbers are not the real colours of their appearances)

3.4. Characterizations

Temperature was linearly increasing form the lab room temperature 20°C to 80°C. As for the frequency, it was set to 10Hz for each test relative to the temperature factor. As for the conductive properties measurement, the applied device is Agilent 34401a digital multimeter. As for the mechanical properties measurement machine, research used Instron 5567 testing machine at room temperature with the aid of standard ASTM D412. The gauge length of the samples is around 20 mm, which is set to stretch at the crosshead speed rate of 10 mm/min until failure. The conductive rubber samples will be tested with vertical clamping. Electrical resistance changing rate was measured after external forcing, which has been tested by maintaining the samples at same extension (Figure 18(a)). As for the stress sensitivity evaluation, the samples will be pressed by the same Instron vertical machine at room temperature. And the deformation rate needs to be set at 0.5 mm/min. By the same method, the machine will be set at the same position. As for the strain sensor test by stretching, the research used the Agilent 34401a multimeter 4-wires resistance testing setting (Figure 18(b)). Test each side of the conductive rubber by the same time, which need to connect the multimeter with PC sites. At the same time, the research connected the Instron 5567 with the same PC sites, which could help us collect data time to time. Furthermore, in order to combine these two functional devices, the research designed a practical software to help. This software is called Agilent 34401A DMM, which take some of useful function from recent version of Agilent multimeter computer used software. Added some computer aid system language order, the software meet the likelihood output.

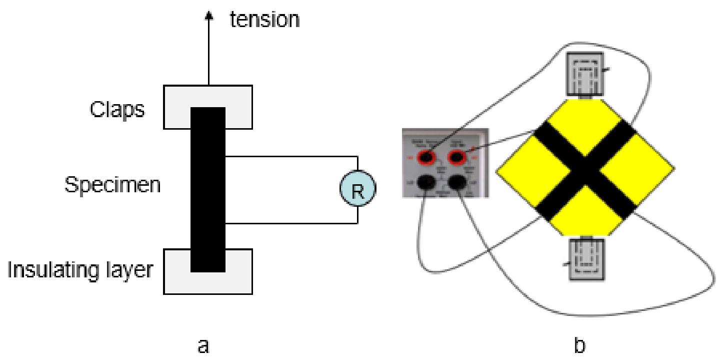

Figure 18. Stretching and compressing test for each specimen

(a for single conductive rubber, b for type I & II strain sensors)

The SEM (scanning electron microscope) images of the conductive rubbers are necessary for characterization. It can represent the microstructure of the conductive rubbers, which can verify our hypothesis and analysis by another perspective. The samples need to cut into proper shape (5mm ×5mm×3mm). This method can indicate the conductive fillers' level of dispersion in polymer matrix.

3.5. Experimental errors' explanation

There will be some experimental errors in our research. Sometimes, these errors are hardly avoided.

The mechanical properties of the polymer decreased after adding conductive fillers. The reasons for phenomenon are various from different perspective. One of the reason is the conductive fillers, which affect the curing functional group working. Furthermore, the manufacturing process might induce some air bubbles into the polymer, which also reduced the mechanical properties. Like the 4.3% CNT conductive rubber, its mechanical performances are worse than other three types. The sticky feeling of 4.3% CNT conductive rubbers are mainly related to the curing functional group in polymer. It affects the polymer curing properly.

The noises for experiment data in strain test are obvious. Due to the stretching process, the polymer-based sensors will have relaxation and deformation. The relaxation and deformation are the natural properties while applying external force. But the deformation within the polymer (molecular level) q cannot change linearly. The crosslinked molecular chains which constructed the polymer will not transmitted in proper ratio. The relaxation property of the polymer can slow down the deformation process. Therefore, the deformation cannot be linear. Another reason for the noises is the testing method. The digital multimeter software can only measure the resistance once per second. Therefore, the data from digital multimeter exist occasional factors. While applying these data into analysing, the data can be fluctuated with few seconds. If the software can monitor the data every 0.01second, the results can be more accuracy.

The resistivity of conductive the testing rubbers are fluctuated while testing. The reasons for this phenomenon are mainly related to the structure and testing method. The resistivities of the testing conductive rubber are collected by digital multimeter. Therefore, the scientific error might occur during the process. The other possible reason for the noise is the sensors' mechanical properties. During the fabricating process, there might be some operational errors. Therefore, the testing materials might not be perfect as our estimation. The irregular edges of the interface for matrix and filler will significant influence on its conductivity performances.

Chapter 4. Result and discussions

4.1. sensing mechanism design

To test the forcing direction and proportional force value, strain sensor need to be capable for collecting forcing data form various direction. As known by the classical mechanical, the external force from random angle can be represented by its separated mechanical performance on each axis (Figure 19).

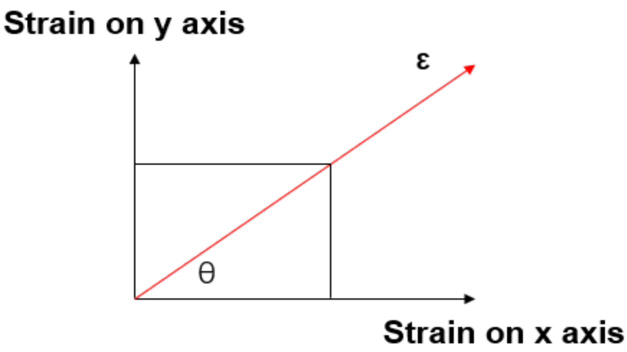

Figure 19. Diagram of the strain separation mechanism

As the force apply on random angle θ, the force can be divided into two direction X axis & Y axis (Figure 19). Generally, the machine can only test the conductivity change rather than forces directly. Due to the external stretching, the sensor will change its shape, which length and thickness change within the process. Within this process, the conductivity of the biosensor will change. The resistances of conductive rubber can use the formulation (1)

$$R = \frac{\rho l}{A} \tag{4-1}$$

(ρ is the electrical resistivity, l is the length of the piece of material, A is the cross-section area of the specimen). Due to the stretching, the shape of conductive material will change it shape, which means the cross-section area will be various within the process. To avoid this issue, this test will calculate base on the volume, which should be constant at the whole time. Therefore, the formulation will change to formulation (2)

$$R = \frac{\rho l^2}{V} \tag{4-2}$$

(V represent the volume of testing material). In order to get the comparation result within this process, the research use the resistance changing rate

$$\frac{R_0}{R} = \frac{\rho_0 {l_0}^2}{V} / \frac{\rho l^2}{V} \tag{4-3}$$

To cancel out electrical resistance ρ, the research need to find the relationship of extension & electrical resistance change. Due to the experiment of 3.5% and 4% CNT conductivity rubber, the conductivity will remain stable at the range of testing distance (0-1 cm) (Figure 20).

As shown by Figure 18, the conduction mechanism in stain sensing is applied from Lin et al (2013). They demonstrate that strain-induced resistivity change can be transform into the fluctuation-induced tunnelling (FIT) model. This model using the increase via the tunnelling gap width through macroscopic separation of the tunnel of CNTs under strain (Lin 2013).

Furthermore, due to this concept, within the composite conductive rubber, the conductive networks are not considered as ideal percolation network. These conductive networks connected within rubber which is the filler are much less than the matrix. Due to this factor, the conductive composites can be thought as infinite conductors (filler) and infinite resistor (matrix). Therefore, the conductivity of the composite conductive rubber dominated by the tunnelling connection of nearby conductive fillers. To fabricate a network to maintain better conductivity, the combination of the conductive filler need to be firm and constant. On the other hand, the conductivity changing rapidly may cause by the leakage of the combination of local conductive fillers. Therefore, the internal resistance of the composite rubber is expected to maintain a logarithmic interrelationship with strain change. And the result tested by vertical stretching machine prove the same theory as Zhang's model.

By using the data from resistivity test (Figure 18), the resistivity of 3.5% conductive rubber and 4.0% conductive rubber can be relative equal to the original one within a proper range. Due to this result, within the equation (3) of $\frac{R_0}{R} = \frac{\rho_0 {l_0}^2}{V} / \frac{\rho l^2}{V}$, the resistivity of ρ and ρ_0 can be approximately equal within the range of 0-1 cm. After this procedure, the resistance changing ratio nearly equal to this equation

$$\frac{R_0}{R} = {l_0}^2/l^2 \tag{4-4}$$

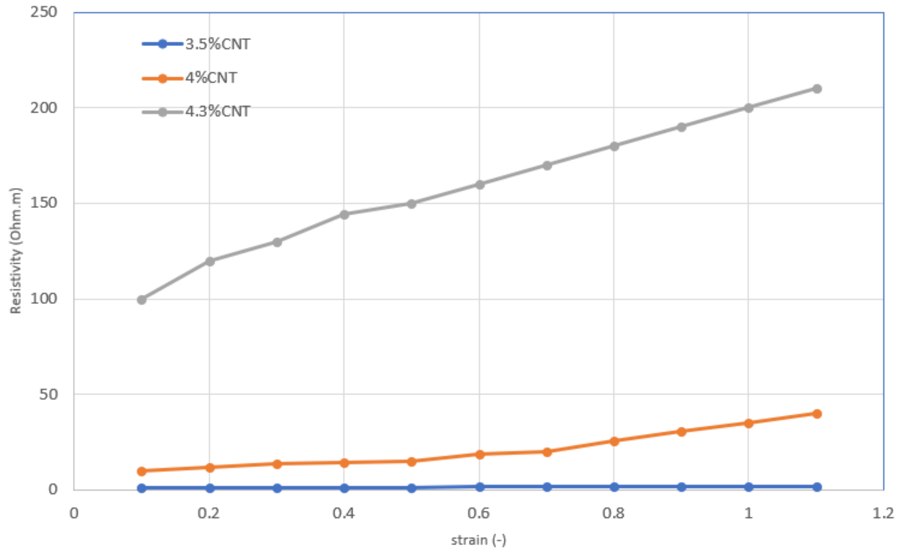

Figure 20. Resistivity verse strain

While testing conductivity change by digital multimeter, the changing distance (ΔL) can be tested through the process. Meanwhile, the strain ε (ΔL/L) can be represented by sensing the conductivity change. Therefore, the divided strain on X axis is $\varepsilon_X = \varepsilon \cos\theta$, while on the Y axis is $\varepsilon_Y = \varepsilon \sin\theta$. By the formulation above, the angle of the strain change can be represented by this formulation:

$$\theta = \tan^{-1}(\varepsilon_Y/\varepsilon_X) = \tan^{-1}(\varepsilon\, sin\theta / \varepsilon \cos\theta) = \tan^{-1}(sin\theta / \cos\theta) = \tan^{-1}(\tan\theta) \tag{4-5}$$

Due to the research of these conductive rubber mechanical properties. within the proper range, the Young's modulus is stable. Within this assumption, the stress (σ) can be represent by the formulation of stress-strain curve. Therefore, the stress direction can be calculated by analysing the data of conductivity change.

4.2. Evaluation of conductive rubber electrical conductive properties

4.2.1. Electrical conductivity calculation method

To get the better conductivity composites rubber, many types of the conductive filler has been tested within the research. Like graphene powder, carbon nanotube (CNT), graphene suspension, carbon nanotube flexible fibers, which have been modified into different phase and state to evaluate the conductive properties. Due to the modification process and product quality, the outcome of the testing conductive filler is not well-behave as the estimation. The acceptable modification results are shown as followed (shown in Table 1). For the given geometry of samples ('l' represents the distance between multimeter electrodes, 'A' represents the cross-section area of testing samples, 'R' represents the resistance of testing samples). The resistivity σ_c of the composites could be calculated as followed:

$$\sigma_c = \frac{1}{\rho} = \frac{1}{R \times A} \tag{4-6}$$

The conductive filler separated into the matrix, which make the composite rubber maintain conductivity. Due the separation factor, the conductivity decrease compared to the purity samples. The samples that used within this process, like Multiwall carbon nanotube (MWCNT), which resistance is around 10 kΩ. As for the graphene NMP suspension, the resistance of dry sample is around 0.5 kΩ, which shown less conductivity performance added into polymer matrix. The result shown as followed indicate some structure issues. The CNT condutive rubber samples catogaries by differet proportion. Before 3.5% of CNT filler, the composite rubber is insulator. After 3.5% of the CNT filler, the composite rubber maintain conductivities. After ratio 4.0% of the CNT filler, the manufaturing process turn harder. Due to the CNT powder adding, the velocity of the mixture decrease. When the ratio reach 4.3% of CNT filler adding, the velocity of mixture is too low to be used for rubber manufactring. After much longer curing period, the mechancial properties for the 4.5% CNT filler conductive rubber are unacceptable for mechanical tesitng. As for the graphene filler conductive rubber fabricaiton issues, the NMP (N-methyl-2-pyrrolidone) residue affect the curing process. Furthermore, due to the less effective dispersion within the mixture, the conductivity properties of the graphene filler conductive rubber need some further treatment to help dispersion. After the ratio of 3.0% graphene filler, the composite rubbers maintain high conductivity.

Table 1. Values for measured resistance and calculated resistivity of different samples (results base on the filler content in phr)

	Average Resistance (MΩ)	Resistivity (Sm^{-1})
3.5% CNT conductive rubber	4.70±0.19	0.0000010
4.0% CNT conductive rubber	0.35±0.06	0.0006
4.3% CNT conductive rubber	0.13±0.03	0.001
3.0% graphene conductive rubber	0.23±0.03	0.0002

4.2.2. Conductive rubber conductive threshold definition

In order to get the most effective phr of the filler within rubber, the research test various ratio of the mixture with conductive rubber. For CNT series, research started with the 3.0% conductive CNT filler (Lin 2013). After curing at room temperature, the conductivity of the composite rubber is nearly zero. Increased the conductive filler ratio to 3.5%, the composite rubber starts to maintain conductivities. With the adding process into the matrix, the material conductivity tends to stable, which fabricating process tend to be complicated. After the whole process finished, the material conductivity threshold curve can be drawn from collected data (Figure 21). According to the logarithm relation calculation, After the 4.3% phr of the conductive filler ratio, the resistivity of the conductive rubber will be stable.

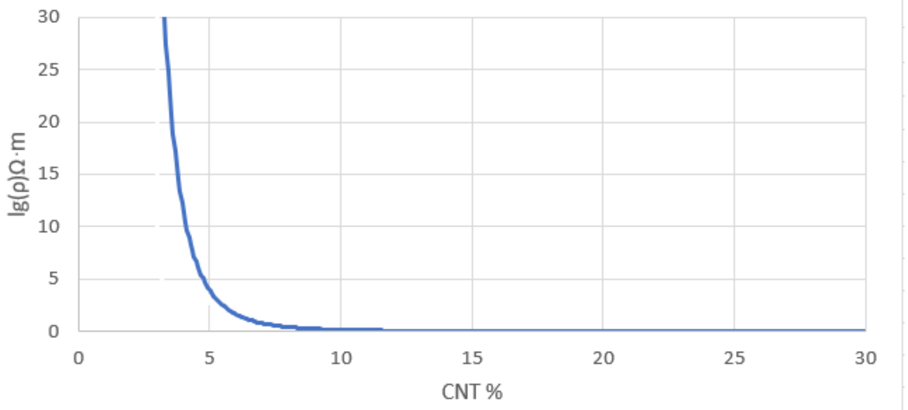

Figure 21. CNT conductive threshold curve

As for the graphene conductive filler, the processes are much complicated than CNT conductive fillers. Due to its complicated fabricating processes, research started with 2% mixing ratio (Shi 2016). When adding to 3.0% ratio of the composite rubber, the material started to maintain conductivities. Due to its less mechanical compliance, the research chooses not to focusing on further conductivity test.

4.2.3. Conductivity change due to strain

The conductivity properties of this research mainly focus on strain-stress process. According to Yang and his team's work, the skin tear rate can reach around 40%. If the strain sensor can be sensitive to this range of skin strain change, the strain sensor will be valid through the test. Therefore, the conductivity performance test within strain-stress curve will be much valuable for strain sensor design, which can prove the valid. By testing different series samples, the analysis resistance changing ratio (R/R_0) verses strain (ε) is represented by these curves (Figure 22).

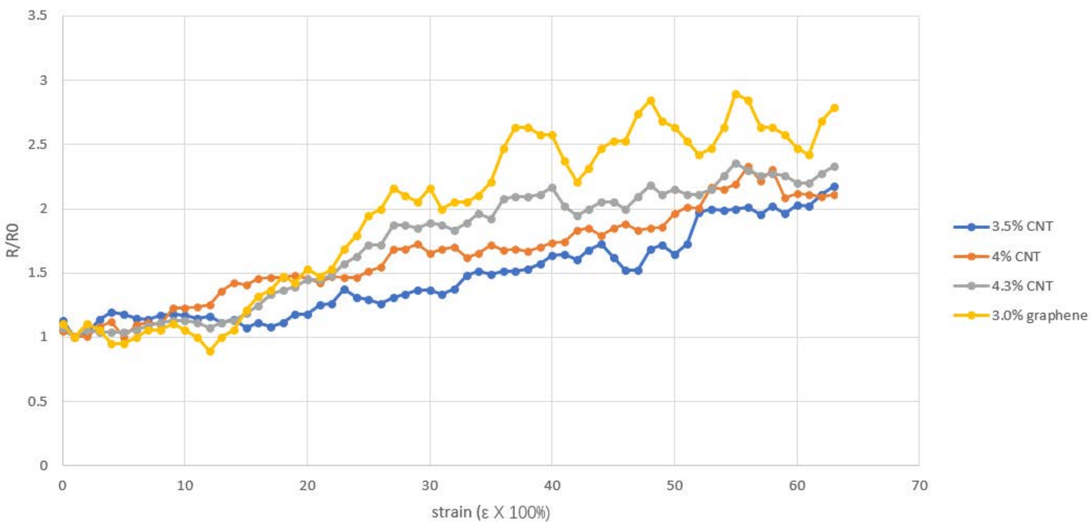

Figure 22. Conductive sensitivity of 3.5%, 4.0%, 4.3% CNT conductive rubber and 3.0% graphene conductive rubber by strain test

As Figure 22 shown, the conductivity changing ratios of 3.5%, 4.0%, 4.3% CNT conductive rubber obtain linear relationship with strain. As for the 3.0% graphene conductive rubber, the curve which indicated the relationship of resistance changing ratio and strain fluctuated, which is not suitable for strain sensor fabrication.

With different ratio of CNT filler and graphene filler, the conductivity changing ration various. All results shown through the curve are average outcome of each series samples (each series have 3 similar samples). The 3.5% CNT conductive rubber shown as blue curve, which conductivity changing slowly by the external extension. After 50% strain change, the conductivity changing much slower than its before. The 4.0% CNT conductive rubber shown as orange curve, which conductivity changing rapidly through extension. After 50% the changing ration of 4.0% CNT conductive rubber increases much higher than before. As for the 4.3% CNT conductive rubber, the conductivity changing much higher than others. After 50% strain change, the 4.3% CNT conductive rubber changing slowly. As for the 3.0% graphene conductive rubber, the conductivity is changing rapidly and fluctuating after 20% strain change.

As we seen through these results, their performance shown by stretching will give better suggestion for further research. Within this section, the 3.5% and 4.0% have better performances while stretching with 10 mm/min. The 4.3% CNT conductive rubber maintain higher sensitivity of strain change, while maintain less continued sensitivity. According to this performance, this type of conductive rubber may have overlap result with other similar conductivity samples, while applying into strain sensor. Therefore, there is a risk of using this type conductive rubber to fabricate strain sensors. Also, the 3.0% graphene conductive rubber maintain over fluctuating sensitivities, which will bring much risk of less-estimated.

Furthermore, within the extension test, the initial sensitivity for each conductive rubber samples are not higher enough to sensing rapid movement. These samples reflect the extension process within few seconds, which shown less change at the beginning. The major reason for this phenomenon is the conductive fillers' types chosen. If the conductive material is metal fiber or powder, the conductive sensitivity and conductivity will be much higher than these results (Allen 2014). Meanwhile, the metal fiber or metal powder may reduce the mechanical properties, like less-flexible. Beside that sensitivity issues, the conductivity changing ratio maintain less linear interrelated with strain change. As for this issue, the major affecting factors belong to the structure and microstructure. In the macro structure, there might be few tiny air bubbles located at the forcing point, which might lead to irregular change within stretching test. Due to the irregular change while stretching, the electrical conductivity and mechanical properties will be affected. In microstructure side, the junction between two conductivity elements may lose connection within stretching. If these conductivity element act like that, the conductivity of the total material may change rapidly.

4.3. Evaluation of conductive rubber mechanical properties

To be able for transforming the strain interrelationship to stress, the Young's modulus is necessary for transforming. Besides that, the other reason for collecting mechanical properties data is to estimate the performance of the conductive rubber applied into the strain sensor (The testing methods is shown as Figure 4a). The strain sensor needs to work on the surface of skin, which means the materials need high flexibility and skin conformity. Therefore, the mechanical properties for both matrix and filler should satisfied these relative requirements. And the average result for all series of samples (Figure 10).

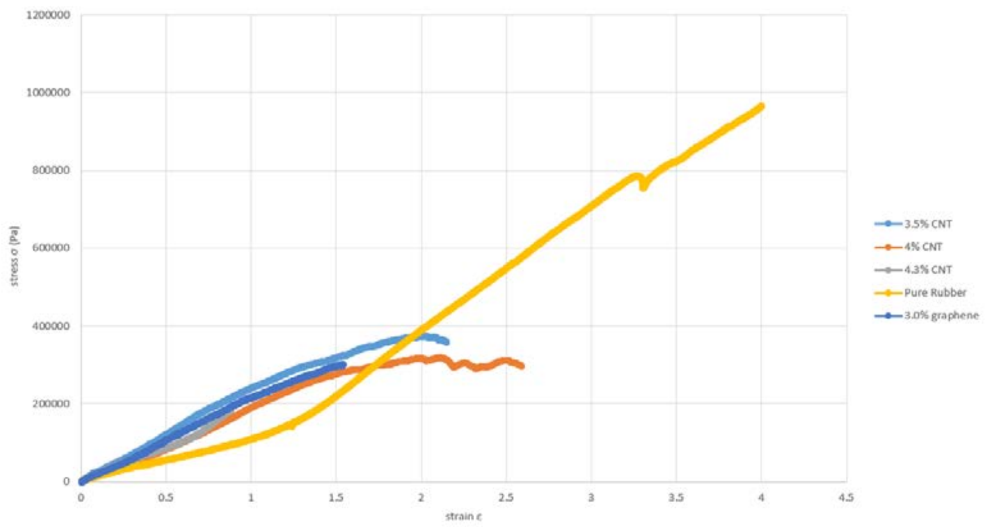

Figure 23. Stress-strain curve for conductive rubber

As it shown, the Young's modulus for conductive materials are linear within the range of 100% strain change (Figure 23). According to literature review, the maximum strain rate of human skin is 40%. Therefore, these conductive materials can work well within skin maximum range. Due to the curve indicated the relationship of stress-strain, the Young's modulus can indicate the elastic properties and rigid level. As shown by the diagram, the original elastomer maintains high flexibility. Furthermore, the fatigue extension is higher enough about 6 times of original size. Compared to original rubber, the conductive rubbers which have been added conductive fillers, maintain less flexibility. Nevertheless, the wear rate become higher. For the 3.5% CNT conductive rubbers, it can bear higher load than other types of the conductive rubber. Also, 3.5% CNT conductive rubber can be extended to 2 times of its original size. Furthermore, the Young's modulus of this type of conductive rubber is higher, which indicated its higher flexibility. As for the 4.0% CNT conductive rubber, it can bear less load than 3.5% CNT conductive rubber. Meanwhile, the relaxation and intensity of the 4.0% CNT conductivity are higher than 3.5% one. And it can be stretched to 2.5 time of its length. As for the 4.3% CNT conductive rubber, which indicated by grey curve shows less intensity and flexibility than 4.0%

CNT conductive rubber. Furthermore, the elastic properties of 4.3% CNT conductive rubber are worse than other two type, which is feeling sticky while touching. Therefore, the 4.3% CNT conductive rubber is not suitable for fabricating strain sensor. As for the graphene filler conductive rubber, its mechanical performances are much similar as 4.3% conductive rubber, which maintain less intensity and flexibility, which might not be a good choice for applying into strain sensor.

All these mechanical performances indicated the potential performances if applied into strain sensor. As these results indicated, the 3.5% & 4.0% CNT conductive rubber may have outstanding performances, if it applied into strain sensor. Furthermore, as seen through the diagram, the contraction area and relaxation area of the conductive rubber is not clear as original rubber. The reason for those samples maintaining this issue might be the structure problem. Within the stretching process, the junction of conductive filler may affect the relaxation process, which might reduce internal properties. Every conductivity joint made by the concentration of conductive materials filler, which influence the mechanical properties of the total environment. After the external stretching, the composite material will change its shape, which will stretch the conductive joint by the same way. Therefore, if there is any concentration of the conductive junction, the mechanical properties will be dramatically affected while stretching.

4.4. Temperature factors for samples conductivity

As mentioned in the introduction part, the temperature effects to the conductivity accountable. Therefore, the conductivity activity with various temperature environment is quite significant to apply into strain sensor. To define the capability of these conductivity rubber performance into various temperature, research used a method to monitor and collect the desired output. Put the samples and testing electrode into the heating oven. Testing the conductivity of the samples through the whole period. To collect the useful data, research mainly focus on temperature that human have. The results are shown in Table 2.

Table 2. Values for measured resistance in different temperatures

	Temperature change (°C)			
	20	37	40	60
3.5% CNT (MΩ)	4.78±0.40	4.82±0.31	4.92±0.41	4.84±0.33
4.0% CNT (MΩ)	0.41±0.16	0.43±0.15	0.38±0.16	0.39±0.18
4.3% CNT (MΩ)	0.12±0.11	0.13±0.15	0.11±0.16	0.16±0.17

As the result shown on the table, the resistance change within 40 degrees is nearly constant. Within heating process, the conductive composites may change the shape and affect the conductivity. While the changing of the internal material is too small which barely ignored. There are some other factors may affect the results shown above. First of all, the shape & size of testing samples affect the final results. If the samples small enough, the conductivity change due to the temperature should be clear. Secondly, the material chosen. The conductive rubber matrix is the functional silicon rubber, which mechanical performance highly sensitive with the environmental temperature. The conductive rubber filler is the carbon nanotube, which is highly sensitive to the environmental temperature. If put them together, the sensitivity should be higher enough to reflect the temperature change. The results show opposite outcome compare to the estimation. The major reason should be related to the temperature range and materials itself.

Furthermore, the material need to be apply on the skin, which need to work within 37 degrees. And the results approve the former estimation.

4.5. Results for strain sensor

The major application of the former experiments' results is to find the suitable methods and materials to fabricate the desired strain sensor. According to former research, the suitable conductivity materials for strain sensor fabrication are the 3.5% CNT conductive rubber and 4.0% CNT conductive rubber. As mentioned above, the strain sensor need to test the direction of force and proportional force. Therefore, the structure design of the strain sensor is defined as the cross section of two slices of conductive rubber. The strain sensors are being divided into two types, according to the applied conductive rubber type. One of them is the combination of 3.5% CNT conductive rubber and 4.0% CNT conductive rubber, which is the type I. The other one is the combination of two 4.0% CNT conductive rubber, which is the type II. The type I does not need to be marked between sides of the conductive rubber, while the type II needs. To evaluate the strain sensor, research test three obvious angles (0°, 45°, 90°). And test one random angle to get the efficiency of the strain sensor.

4.5.1. Type I strain sensors experiments

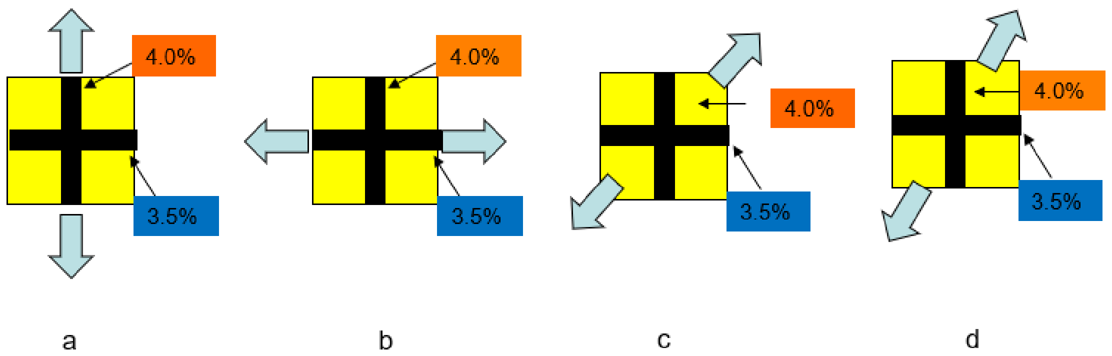

Figure 24. Different angle of strain sensor

(a indicated 0°, b indicated 90°, c indicated 45°, d indicated the random degree)

4.5.1.1. Type I strain sensor evaluation by 0° stretching

First of all, evaluating the strain sensor by the angle of 0° (Figure 11(a)). As shown through the diagram, the testing sensor is clap by the vertical stretching machine. With the stretching by the machine, the mechanical properties and conductivity change shown by Figure 25 and 26.

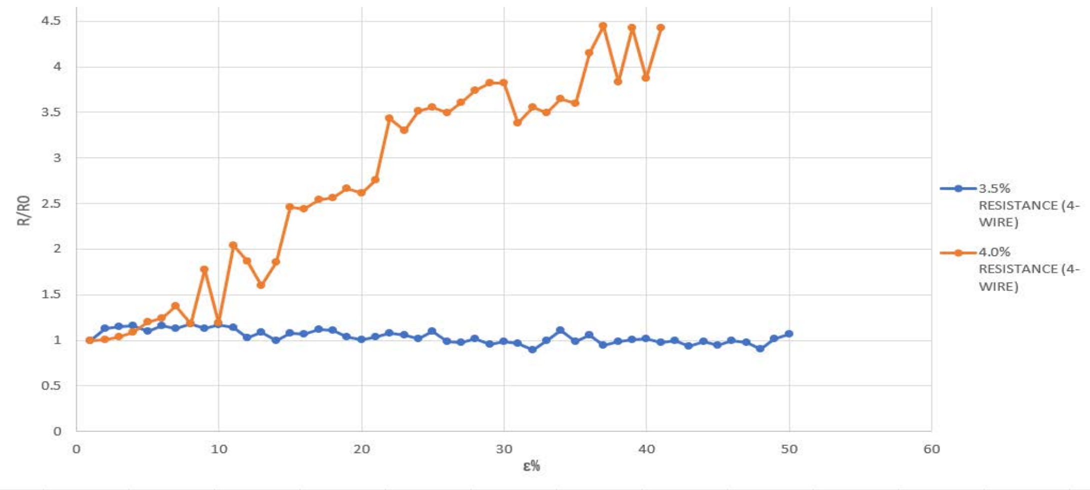

Figure 25. changing ratio verses strain change of 0° direction stretching

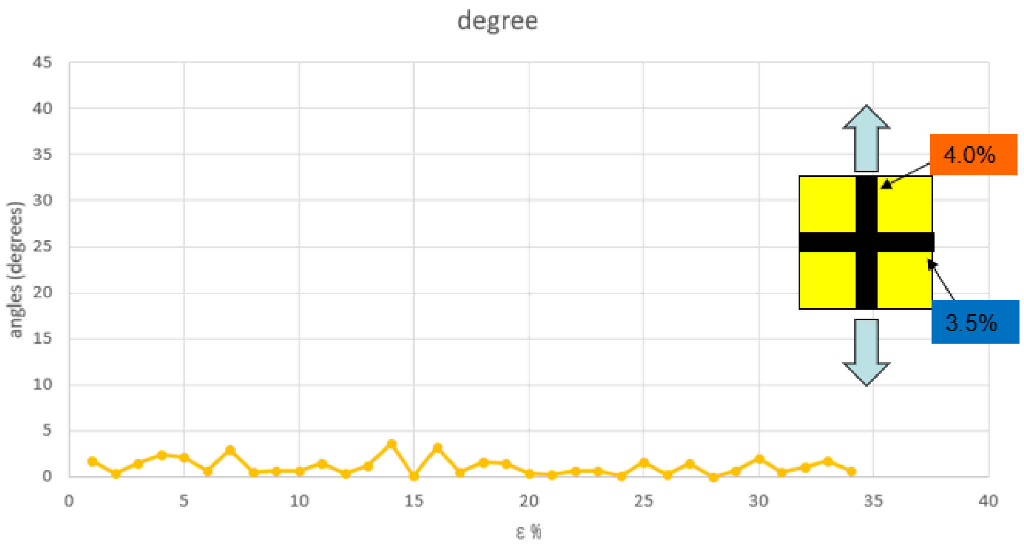

Figure 26. Angle analysis of the 0° direction stretching

As it shown (Figure 25), these two types of the conductive rubber have different performances. The blue curve represents the 3.5% CNT conductive rubber, which barely change by the stretching. While the 4.0% CNT conductive rubber changing rapidly due to the stretching of testing machine. The resistance changing ratio of the 4.0% conductive rubber increase dramatically. After 50% strain change (stretched to 0.5 times of its original length), the resistance changing ratio increases slowly. Within the whole period, the sensor behaves as the research needs. The strain sensor was being stretching to 0.5 times of its original length, which within the estimation of the stable resistivity. Therefore, after analysing the data, the angle of the testing direction is shown by Figure 26. As it shown, the angle of the testing direction is around 1 degrees, which is slightly different with our setting. The reason of this fluctuate output shown by Figure 26, might be related to the fluctuate conductivity and sensor relaxation. If the conductive rubber enforcement with metal particles, which conductivity will be much reliable and stable. If so, the conductive composites rubber will lose much flexibility and skin conformity.

While testing the strain sensor, the external testing wires may increase the deformation of the sensor. Due to this factor, the mechanical properties of strain change reduced. To filter out this side factor, the research used light conductive wires and conductive glue to complete the testing procedure. Nevertheless, besides that point, there is a thick film between two types of the conductive rubber which avoid connecting problem while setting.

4.5.1.1. Type I strain sensor evaluation by 90° stretching

Then, the research did the 90° stretching evaluation of the strain sensor. Compared to the first evaluation, the 3.5% CNT conductive rubber is directly stretching through the process at this time (Figure 27).

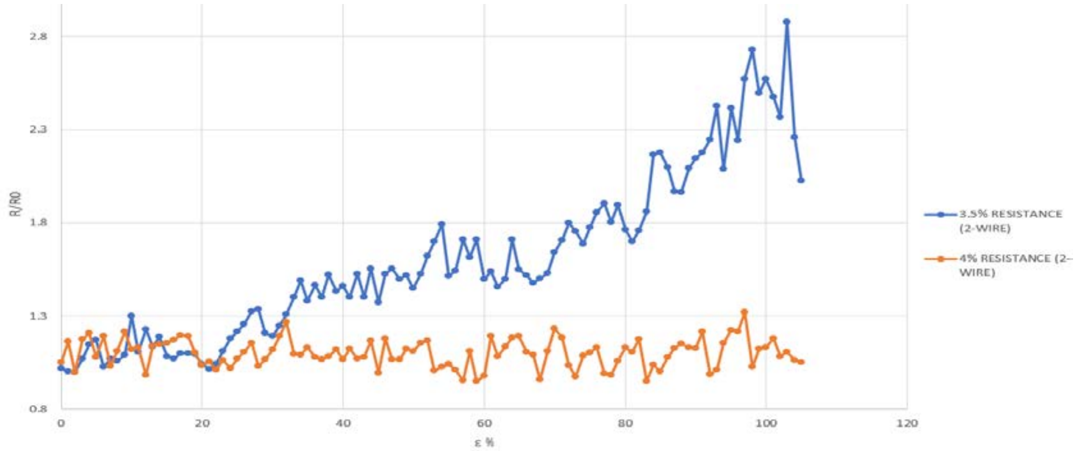

Figure 27. Resistance changing ratio verses strain change of 90° direction stretching

As it shown (Figure 27), the mechanical performances for these two types are directly opposite compared to 0° stretching. The 3.5% CNT conductive rubber shown by the blue curve, indicated the stretching applied on the horizontal side of the sensor (Figure 24(b)). While stretching the 3.5% CNT conductive rubber, the other type of the conductive filler barely changes. As the result shown by Figure 27, the orange curve represents the 4.0% CNT conductive rubber performances, which barely change while stretching. As for the 3.5% CNT conductive rubber, the conductive changing ratio slightly changes before 20% stretching. After 20% stretching, its elastic properties changing rapidly. After 80% stretching, the conductive changing ratio changing irregular, which indicated the mechanical and conductive properties out of order. Compared to former estimation, the resistivity of conductive rubber within 0.8 times of its original length is relatively equal to the resistivity without stretching. Therefore, the result meets the former estimation. On the other hand, the performance of the 4.0% CNT conductive rubber shown high sensitivity to the strain change. And it barely changes while 3.5% CNT conductive rubber stretching. After analysing the data with the formulation above, the angle of the force direction shown by Figure 28.

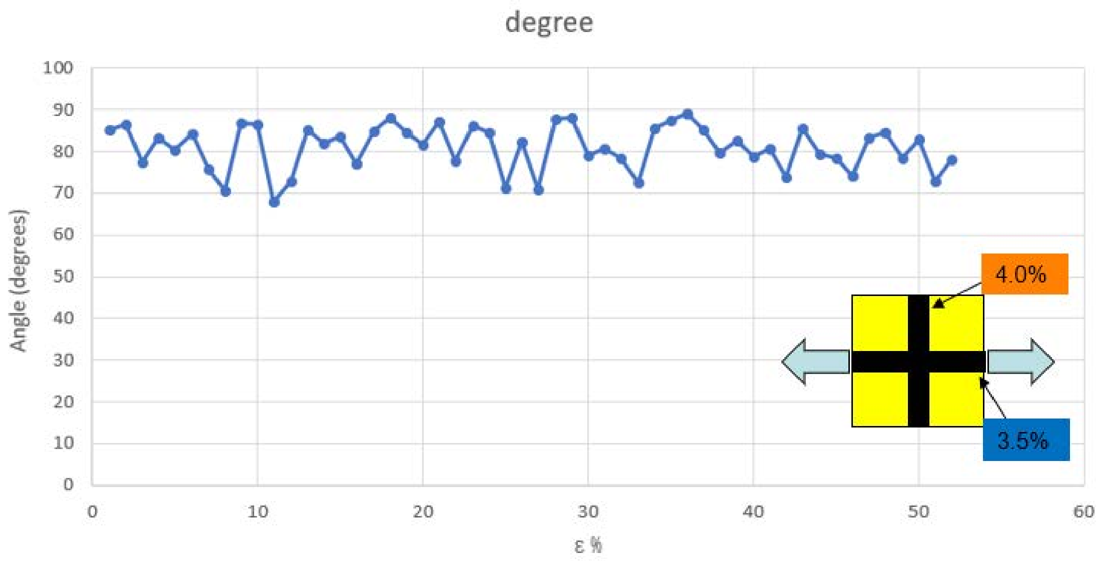

Figure 28. Angle analysis of the 90° direction stretching

As it shown (Figure 28), the testing angle is around 80 degrees. Compared to the vertical stretching, horizontal evaluation show less accuracy. Due to the result from same series of samples, the mechanical properties should be the same. Meanwhile, the differences between these two evaluations indicated the sensitivity between 3.5% CNT conductive rubber and 4.0% one. Due the less sensitivity of the 3.5% CNT conductive rubber, the network combined with 3.5% and 4.0% CNT conductive rubber can be easily recognized. Meanwhile, the less sensitivity of the 3.5% CNT conductive rubber may lead to inaccuracy of the strain sensor. For some micro motions, which appears rapidly may lose traction. For further experiment to fix this issue, the strain sensor may improve by the high-quality conductivity fillers or changing the conductive filler phr. These solutions may improve the device accuracy, which need further experiment data to approve.

4.5.1.1. Type I strain sensor evaluation by 45° stretching

Then the research does the third evaluation with the angle of 45 degrees. This type evaluation is to confirm the combination function of these two type of CNT conductive rubber. Although the former two evaluations are also related to these two type of evaluation, the middle point testing would highly reflect the sensitivity and reliability of the strain sensor. Therefore, the stain sensor has been tested with the same procedures above. The stain sensor was clipped by vertical stretching machine as the diagram of Figure 9(c) Due to this clipping gesture, the wires connected to strain sensor will not be affected by vertical stretching machine. Therefore, the evaluating result will be much accuracy than former evaluation. The mechanical properties can be tested within the process (Figure 29).

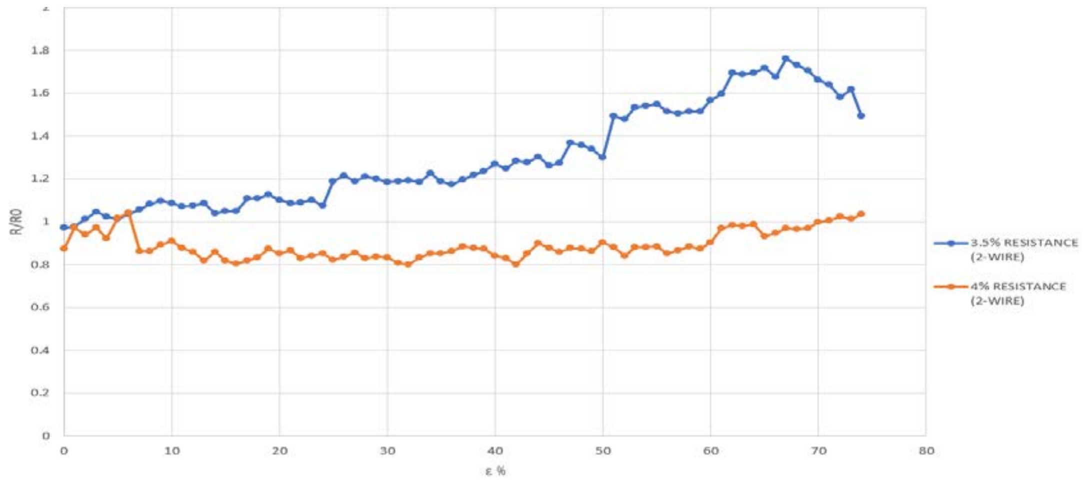

Figure 29. Resistance changing ratio verses strain change of 45° direction stretching

As it shown (Figure 29), the 3.5% CNT conductive rubber behave better than former evaluation, which represented by the blue curve. The resistance changing ration increase rapidly. After the 65% of extension rate, its sensitivity started to decrease, which will not efficiently reflect the testing angle. As for the 4.0% CNT conductive rubber performances, the conduct sensitivity seems less efficient than 3.5% one, which represented by orange curve. The reaction for the 4.0% CNT conductive rubber seems to be fluctuated. The reason caused this phenomenon might relate to the structure problem, and scientific errors. Although the results are the average one among this series, there still might be some handling operation errors. Within the range of estimated model, the resistivity can be cancel out. Applied the data into the calculation model, the angle of the force direction shown by the curve (Figure 30).

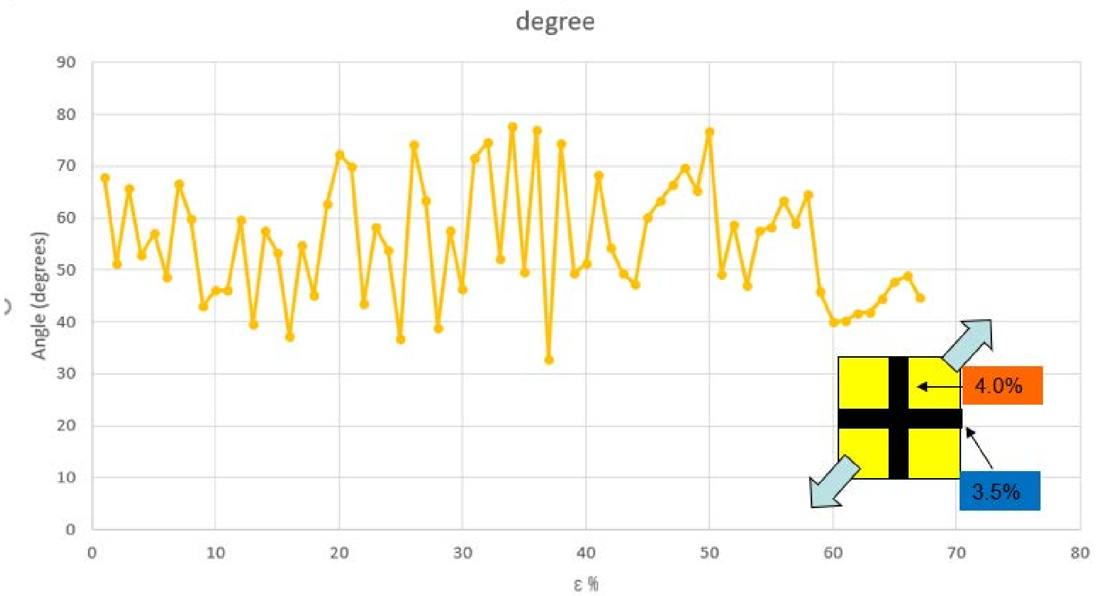

Figure 30. Angle analysis of the 45° direction stretching

As the figure indicated, the force direction is around 50 degrees. As the research setting, the force direction is 45 degrees, which is bit difference than the output. Furthermore, the angle testing system get the data fluctuated, which reduced the accuracy. According to this issue, the research found some useful suggestions. (1) the conductive rubber sensitivities reduced dramatically with distance from conductive layer increasing. (2) If the forcing point distance between conductive part, the stability of testing system reduces. The results tend to be fluctuate. (3) the length of effective conductive rubber affects the accuracy. (4) the microstructure transformation lead to macrostructure change fluctuated rather than linear. (5) the density of conductive network will highly significant for testing system reliability.

Besides those helpful feedback through this evaluation, the subjective factors made the result complicated, which hardly explain by simple reason.

4.5.1.1. Type I strain sensor test by random angle stretching

Finally, the experiment come to the testing part. To avoid accidental event, the research chooses random angle which applied on clipping machine. Then, taking a picture of the random angle to act as a proof (Figure 24(d)). After connecting all devices to collect data, the test followed all the procedure that used in former evaluation. The result is shown in Figure 31.

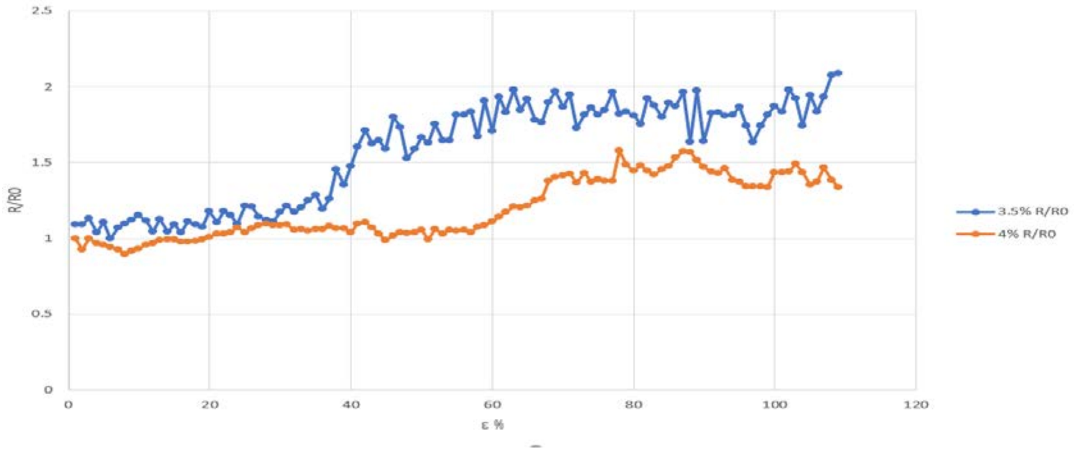

Figure 31. Resistance changing ratio verses strain change of random angle direction stretching

According to the diagram shown in Figure 31, the 3.5% CNT conductive rubber represents by blue curve shows rapidly increase of the resistance changing ratio via stretching. After 60% of the stretching process, the resistance changing ratio increases slowly, turned to stable. As for the 4.0% CNT conductive rubber, which represents by orange curve indicated the slightly increases of resistance changing ratio. At the beginning of the monitoring, these two types of conductive filler reacted slowly. Furthermore, their stretching process mainly around 50% to 60%, which means the data can use the calculation model mentioned before. Therefore, analysing the collected data and transform to desired output (Figure 32).

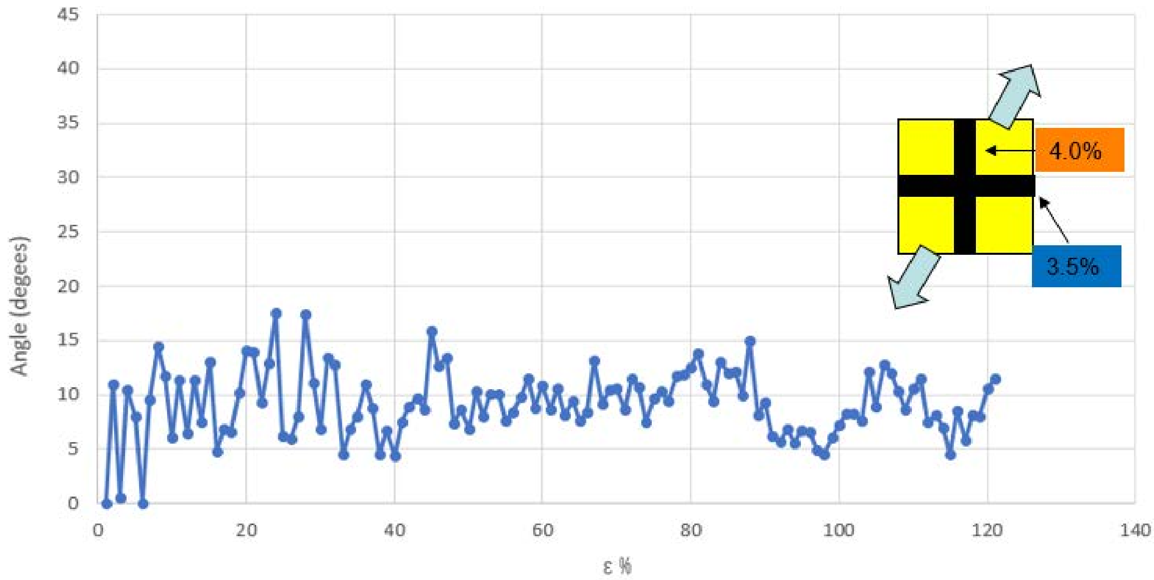

Figure 32. Angle analysis of the random angle direction stretching

As it shown (Figure 32), the result shows a relative stable result around 10 degrees, which is much similar with the random position (Figure 24(d)). Apart from the final result, the performances of the two conductive layers are sensitive enough to monitor the angle of stretching direction. Although the result is bit fluctuating within the process, the outcome is clear enough to be used.

According to the evaluation and test results, here is some results seems from the experiment. (1) Compared to 45 ° direction evaluation, the strain sensor would like to be much sensitive if the testing point near the conductive layers. (2) At the beginning test of the research, the sensitivity is less qualified enough to behave immediately. (3) the conductivity of the conductive layers is fluctuated within the experiment. (4) the micro structure may give the reason to some of the irregular performance of the strain sensor. (5) By the same time, after long time testing, strain sensor still maintains high quality (low fatigue rate).

4.5.2. Type II strain sensor

The other type of the strain sensor is the combination of two 4% CNT conductive rubber. The reason to design this type of the strain sensor is to collect the data for comparing test of various sensitivity conductive system outcome. Based on this theory, the research followed the former procedure and fabricated the type II strain sensor. And test the type II strain sensor with the same devices, software, and procedures. Base on the results from type I strain sensor, the vertical and horizontal direction evaluation indicated that these two direction maintains high sensitivities. Therefore, the type II strain sensor mainly focus on random angle and the forcing point far from the conductive layers. To approach these requirements, the test focus on random angle and diagonal direction, the designed sensor is shown in Figure 33.

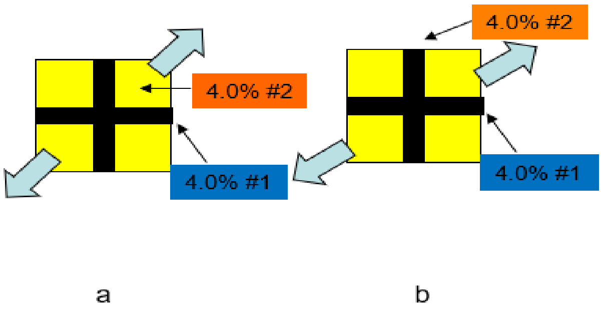

Figure 33. Type II strain sensor tests

(a indicated 45° test, b indicated random angle test)

As it shown (Figure 33), the type II strain sensor mainly focus on these two types of test.

4.5.2.1. Type II strain sensor evaluation by 45° stretching

First of all, the type II strain sensor was being set as diagonal directions, as Figure 33a shown. Due to the type II strain sensor fabricated by two 4.0% CNT conductive rubber, the sensitivity of this type strain sensor should be higher than type I. Based on this assumption, the results of type II strain sensor will be analysis compared to the results of type I. The results are shown in Figure 33.

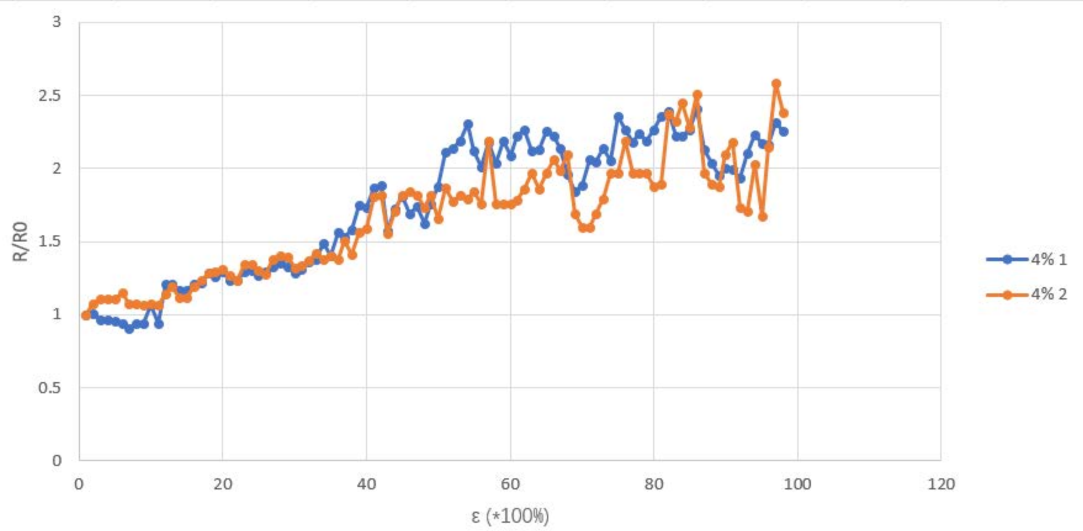

Figure 34. Resistance changing ratio verses strain change of 45 ° direction stretching

As it shown (Figure 34), the type II strain sensor sensitivity increase rapidly. The #1 4.0% CNT conductive rubber shown as blue curve sensing the strain change immediately. And the changing ratio of conductive rubber increase slowly. As for the #2 4.0% CNT conductive rubber represented by orange curve. #2 4.0% CNT conductive rubber's resistance changing ration increase rapidly with external stretching. Meanwhile, after 60% stretching, the resistance changing ratio highly fluctuated. Therefore, within 60% stretching ratio, the data can be input into the model that used in type I strain sensor analysis. The result is shown in Figure 35.

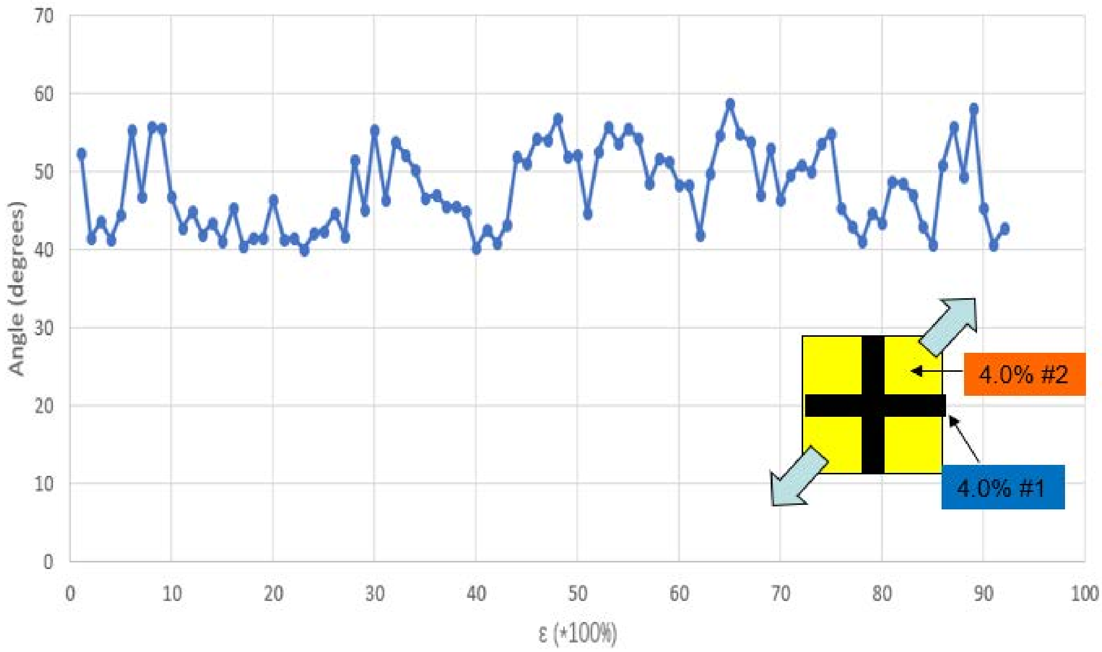

Figure 35. Angle analysis of the 45° direction stretching

As it shown (Figure 35), the angle of the stretching direction is located around 48 degrees, which maintain less fluctuation. Furthermore, the sensitivities of the type II strain sensor are effective to monitor the stretching angle. Meanwhile, there is still some fluctuation within monitoring process. It might be the factors of the conductive filler, which play the major role in monitoring process. Compared to Figure 30 (45° stretching of type I strain sensor), the sensitivities and stabilities of type II strain sensors are highly improved from type I. Therefore, the improvement of the conductivity of monitoring network will gain much benefits if applied on clinical use.

4.5.2.1. Type II strain sensor test by random angle stretching

Secondly, the research applied random angle test on type II strain sensor (Figure 33(b)). The type II strain sensor need to be set as the diagram shown. With the same procedure, the research collected the data and get the results (Figure 36).

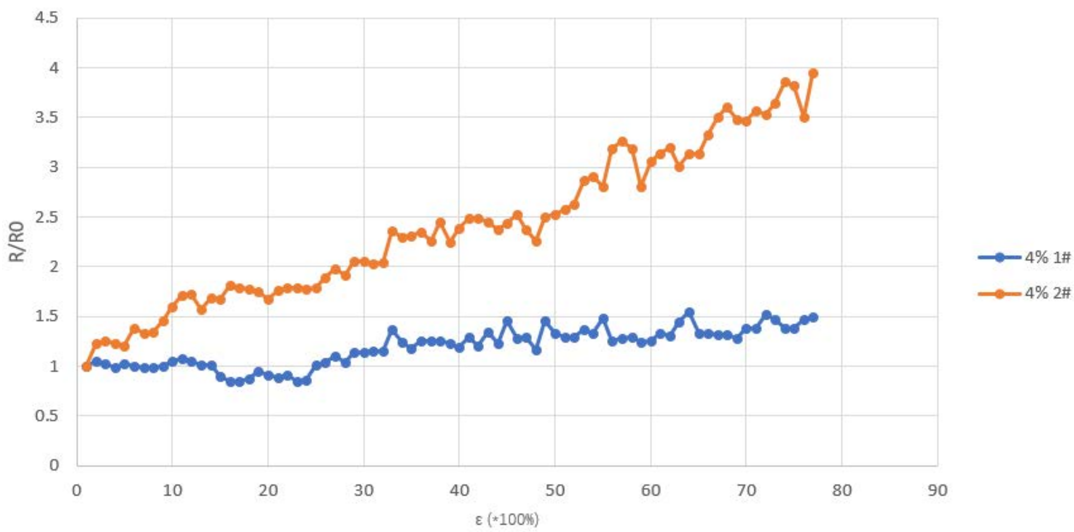

Figure 36. Resistance changing ratio verses strain change of

random angle direction stretching

As Figure 36 indicated, the #2 conductive layer resistance changing ratio increase rapidly with external stretching. Furthermore, the resistance changing ratio of #2 conductive layer increase without rapid fluctuation. The relationship between strain and resistance changing ratio stable and accuracy. As for the #1 conductive layer, the changing ratio of resistance increase slowly. At around 65% of stretching ratio, the changing ratio tend to stable, which indicated the angle near to the #2 conductive layer. The reason for this assumption based on former research. Within the former research, if the stretching direction close to any one of the conductive layer, the resistance changing ratio would increase dramatically compared to the other. Due to the reliable stretching changing ratio within 60%, which can be calculated with the model mentioned above. The output result of the stretching angle monitoring (Figure 37).

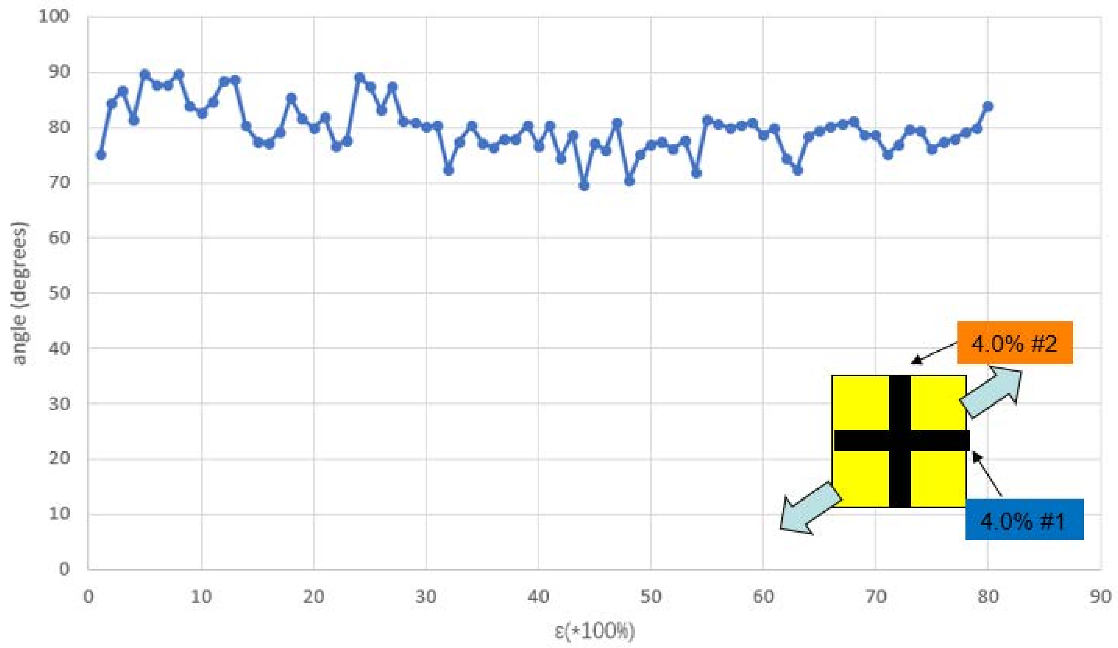

Figure 37. Angle analysis of the random angle direction stretching

From the result (Figure 37), the angle of the type II strain sensor stretching direction is apparently located at around 80°. Compared to the testing position (Figure 33(b)), the monitoring result is reliable. Furthermore, according to Figure 36, the stretching point might close to the #2 conductive layer. Therefore, the results can prove all estimation. Meanwhile, the results of the angle monitoring fluctuated within the range of 20 degrees, which still need to improve the accuracy.

Based on type II strain sensors behaviours, there are some remaining issues need to be considered. (1) If increase the conductivity of the strain sensor monitoring network, the maximum conductivity outcome that the strain sensor can get. (2) Based on the recent results, the angle monitoring accuracy can maintain within 20 degrees. If increase the conductivity of the sensing network, the deviation of the accuracy can be kept within the minimum range. (3) With the increasing the conductivity of sensing network, the mechanical properties and skin conformity less competitiveness. (4) The research also focuses on the network constructed. If the network combined each other, which could increase sensing area. Meanwhile, the interaction of each elements may affect the final accuracy, like deviation increasing.

Chapter 5. Further work

Due to length of the research periods, only the feasibility study has been conducted. Research is going to design a strain sensor which can sensing strain change & force angle on the human skin. According to the research, the type II strain sensors' performances are better than type I strain sensors. To make this system more reliable, the research needs further treatment to the strain sensors. If the research wants to get the guide of sensors' improvement, it needs to compare with other relative researches to find the leakage. Therefore, some of the tasks need to be further researched, after comparing with others.

(1) The further work will focus on improving the conductivity of conductive rubber.
To improve the reliability of the system, further work will improve the conductivity and mechanical quality of conductive rubber. The new conductive rubber will base on two fields, CNT fillers and hyper particles fillers. There will be metal particles and CNT powder into the hyper particles, which will highly increase the conductivities properties. As for the CNT conductive fillers, to improve the conductivities without increasing the content, it needs further treatment. According to Allen (2014) and his team's work (they fabricated the conductive hyper CNT fiber), the CNT conductivity can be improved by further treatment (Figure 38). Based on their research, the conductive materials they used are better than our strain sensors. Therefore, further research should focus on hyper-phase conductive rubber.

film	CNT G^+ upshift (cm^{-1})	average R_S ($\Omega/\square$)	%T at 550 nm	$\sigma_{DC}/\sigma_{optical}$	conductivity (S/cm)
SWNT/P3HT doped	1.52	500	88	5.6	1300
SWNT/P3HT/PPy 1/1/4 dry[a]	3.14	240	88	11	1700
SWNT/P3HT/PPy 1/1/40 dry	4.88	93	68	9.6	2800
SWNT/P3HT/PPy 1/1/40 wet[b]	9.75	290	83	6.5	1000
SWNT/P3HT/PEDOT 1/1/4 dry	3.68	170	82	11	2100
SWNT/P3HT/PEDOT 1/1/40 dry	4.66	85	71	12	3300
SWNT/P3HT/PEDOT 1/1/40 wet	7.37	340	79	4.4	770

[a]Solvent was evaporated before immersion into ferric chloride solution. [b]Solvent was not evaporated before immersion into ferric chloride solution.

Figure 38. Raman Peak Shifts (in cm^{-1}) and transparent electrode performance for various SWCNT-Conjugated polymer films (Allen 2014)

If the CNT can combine with some metal particles, the conductivity sensitivity will increase dramatically (Lin 2013). As it shown (Figure 39), the resistivity increases dramatically within small strain change, which indicated the sensitivity of the composites.

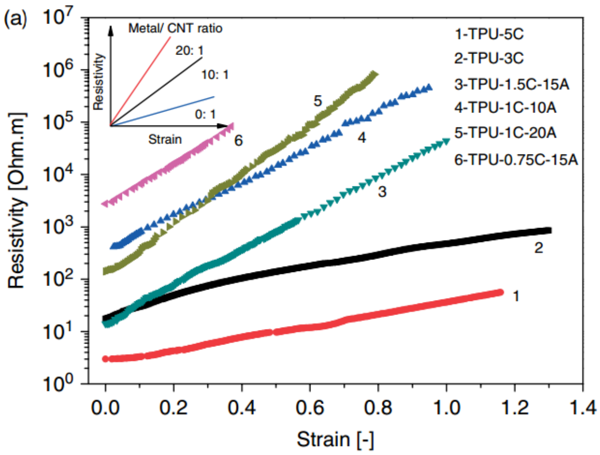

Figure 39. Resistivity versus strain in TPU composites (PU represents TPU, C represents MWCNT, A represents eutectic alloy) (Lin 2013)

As for this segment, the major challenge is to improve the conductivities and balance the mechanical properties. According to Lin's work, our research will add some metal particles into conductive materials to improve the conductivities. Therefore, further research will focus on balancing the mechanical properties and conductive properties by ingredient ratio controlling.

(2) The further research will construct a network to sense the force direction and proportional strength.

If the sensing network establishment, which combined each sensing element (research in this study) will be quite significant. The major part for this segment is to balance the deviation of combining each element, which might be a huge amount of the calculation. In recent research, the combining two element sensors are being studied. To establish an efficient network, the research need computer aid and advance digital multimeter to collect data.

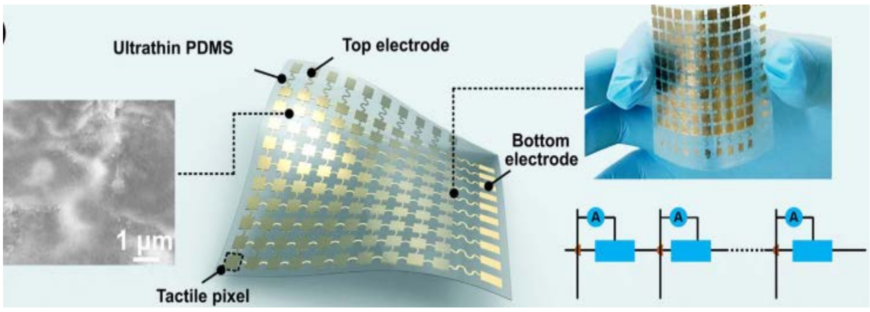

Figure 40. Illustration of an ultrasthin and flexible sensor array with 10X10 pixels. (left) FESEM image of flexible PANI-HNSC. (right) Schematic illustration (top) and circuit diagram(bottom) (Lou 2017)

As it shown (Figure 40), Lou (2017) and his team use additional circuit to connect each junction. They used the colour matching system to indicate the pressure applied over the sensor surface (Figure 41). They cannot calculate each isolated element individually. Therefore, our research need to consider about the method to represent the outcome by balancing each other.

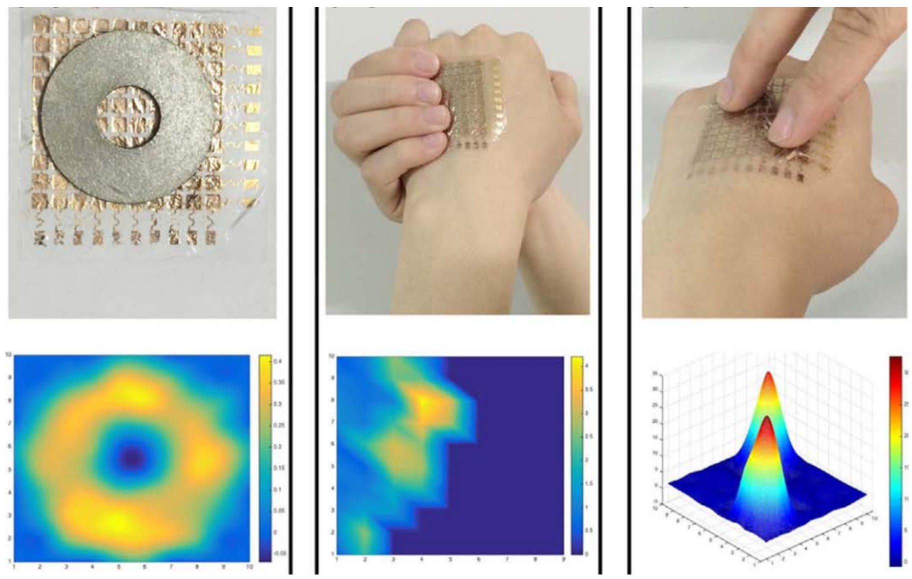

Figure 41. Diagram of the sensing result of pressure apply on the sensor and the colour matching system indicated the pressure level (Lou 207)

According to their experiment, their sensors' sensitivities are outstanding than other. Therefore, the further research will base on those concepts to build a network to monitor the strain.

(3) Future work will improve the strain sensitivity of the sensors.

This research fabricated the strain sensor, which can be used for sensing the proportional stress and stretching direction. Meanwhile, the accuracy for both requirements have not been satisfied. Therefore, the strain sensor need to find other methods to improve the sensitivities of the strain sensor. It can be solved by improving the conductive fillers or changing the sensor structure. If the conductive filler can be improved like Lin's work (Figure 38) the sensitivity can be largely increased. If the structure can be increased like Lou's work (Figure 40), the skin attachable can be highly increased, as well as the sensitivity.

(4) A remaining experiment needs to complete in future work, which called the visible strain simulator.

This device is combined with LED light, strain sensor made in this research, and the common mode gain part, which designed to be sensitive for the strain change. With the stretching of the strain sensor, each side of the LED light flashing or changing their brightness through the process. Due to the high resistance of the conductive fillers, the brightness of the LED light is less efficient for detecting strain change. To amplify the signal of stretching process, it needs to design an amplifier circuit to increase the output signal (Figure 42).

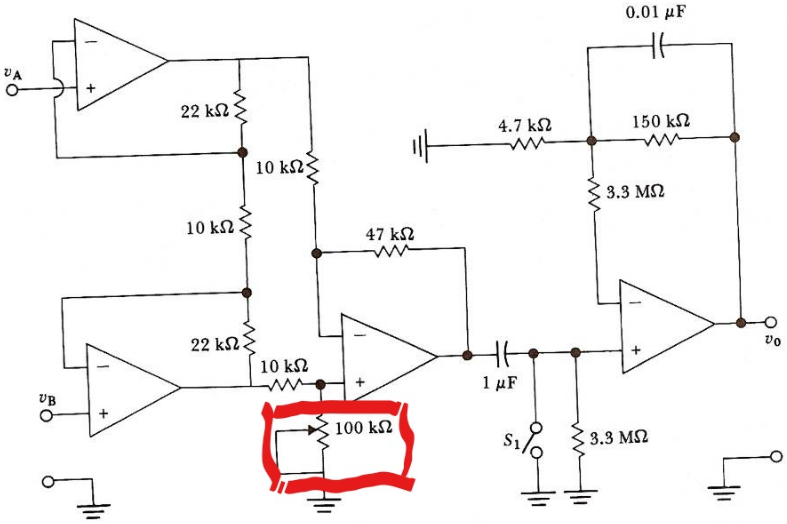

Figure 42. Amplifier circuit design for increasing signal

As it shown (Figure 42), the red part which is adjusted resistor will be replaced by fabricated electrical conductive rubber slice. And the Vo part will connect to the LED light. After testing this prototype circuit, the brightness was not met the desired requirements. Therefore, further exploration of the circuits design to make sure of the efficiency in monitoring process.

(5) The application of this strain sensor. The further research will focus on building wounding healing monitor, or artificial intelligence robot artificial skin.

Based on beginning plan, this type strain sensor will be applied onto the surface of human skin. Therefore, the further research focal point will be mainly at this application. To sensing the force direction and proportional strength can provide a feedback loop to the artificial intelligent robot or other devices (Figure 43). Furthermore, this strain sensor may apply onto the wound healing monitors, which provide useful suggestion on further recovery processes. Therefore, this type of strain sensor needs to be completely considered with various aspects that can be use in any conditions.

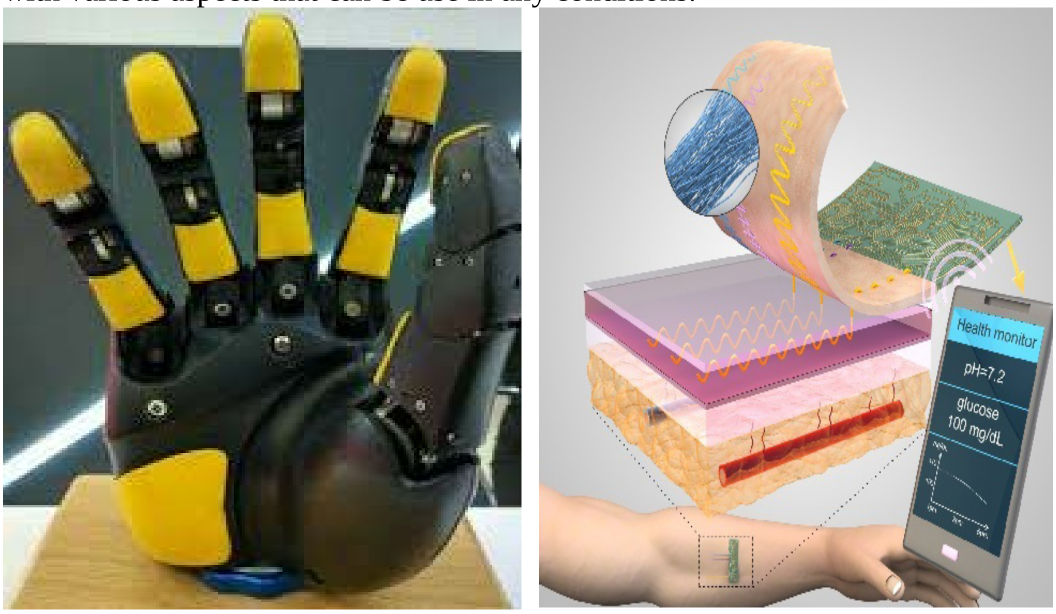

Figure 43. Further experiment on artificial intelligent and wound healing monitoring (Zhang 2017)

Chapter 6. Conclusion

The following conclusions can be drawn from this feasibility study.

(1) A sufficient dispersion of carbon nanotube (CNT) and graphene in polydimethylsiloxane (PDMS) leads to well-behaved conductive composites. With precise procedures, the research fabricated four types of the conductive rubber, i.e., 3.5%, 4.0%, 4.3% CNT conductive rubbers, and 3.0% graphene conductive rubber. Due to the special fabricating process and cooperative conductive filler, the composites maintain high electrical conductivities and outstanding sensitivities for tension. As for the conductive rubber, the resistivity for each of them is various. The 4.3% CNT conductive rubber maintains the best conductivity of these four of conductive rubbers, while the 3.5% CNT conductive rubber is the lowest. Furthermore, the temperature and force factors are also researched.

(2) The mechanical properties for those four types of the electrical conductive rubber are shown by the stress-strain curves. Their Young's modulus within 100% stretching are nearly constant. Therefore, the conductive rubber strain change can be linked to stress change. Moreover, their elastic properties relatively reduced by adding multiple phr conductive fillers into the system.

(3) With the temperature increased, the electrical conductivity of the conductive rubber relative remained stable. Due to their working position (human skin), the electrical conductivity for these conductive rubbers remained stable at 37-40 degrees.

(4) The strain sensor which is fabricated by 3.5%, 4.0% CNT conductive rubber and PDMS, can be used for monitoring the direction of external force. There are two types of the strain sensor that have been researched. For both type of the strain sensor, the direction of external stretching can be monitored, which proved the estimation of the beginning plan. As for the type I strain sensor, it shows high quality sensitiveness in the vertical direction, the horizontal direction, and the angle closed to them. After evaluation of the type I strain sensor in 0°, 90° and 45°, a random angle test will be applied on it. While for the type II strain sensor, it maintains highly sensitive to various angle compared to that of type I. To test the type II strain sensor, the research design 45° and random angle direction test on it. Furthermore, both strain sensors maintain outstanding mechanical properties, which meets the requirements of high flexibility and skin-conformity.

(5) The sensitivity of the type II strain sensor is much higher than that of the type I strain sensor. Furthermore, the performances for both of them while monitoring the stretching process are in a high quality if stretching points closed to conductive sensing network. If the stretching points are far from the sensing network, the monitoring performances are in less quality.

(6) Further exploration on strain sensor will be focus on conductive network constructing, highly conductive rubber fabricating, and practical application testing.

Appendix

Supporting information for experiment

During the fabricating process, the major device is material homogenization (Figure A1) machine which used to make uniform mixture.

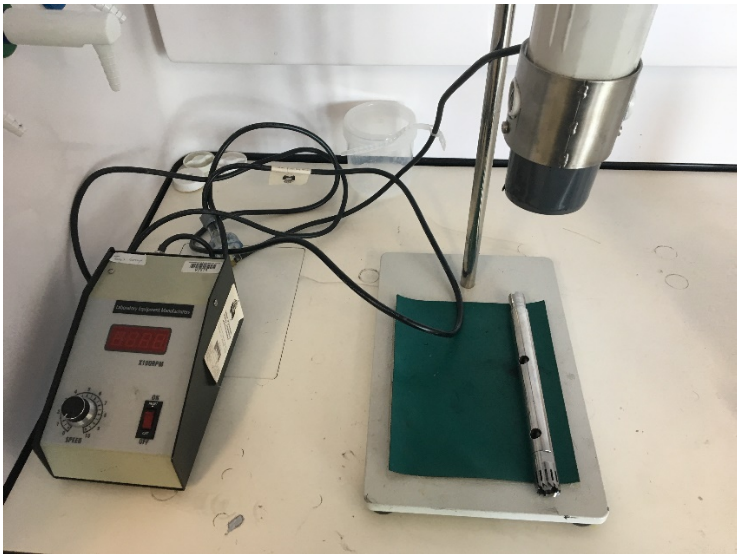

Figure A1: Homogenization machine

This device is using shear stress to mix the organic solution. The metal stick need to connect to the engine, which control by the visual manual controller. Shearing rate is 35-40 X 100RPM in general. According to the solusion viscosity, the shearing rate can be various.
Combined with ultrasonic machine (Figure A2), the homogenization machine can disperse the solution properly. The ultrasonic machine is the general type.

Figure A2: Ultrasonic machine

During the ultrasonic bath, the materials should be covered with plastic wrap. Therefore, the materials can isolate form the bath water. And the temperature of the ultrasonic bath is the other factor affected the results. The temperature will increase during the process, which should be controlled around room temperature. Time should be controlled within 1hour.
Furthermore, we applied the magnetic rotor stirring system (Figure A3) to help the solution uniform.

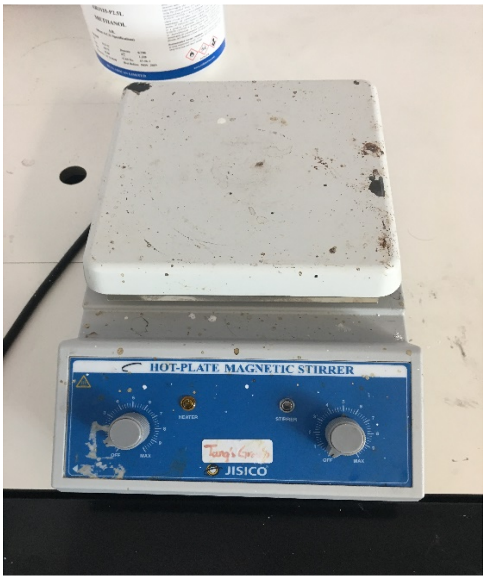

Figure A3: Magnetic rotor stirring

The magnetic rotor need to put into the solution. Therefore, the rotor chosen is one of the important issue. We try different sizes of the rotors into beakers to get the suitable one. And the stirring speed should be controlled based on the viscosity (generally used the speed within 3-3.6).

Then, we used the oven to treat the solution. We used a pump to vacuum the laboratory oven (Figure A4) and get rid of the additional organic solvent.

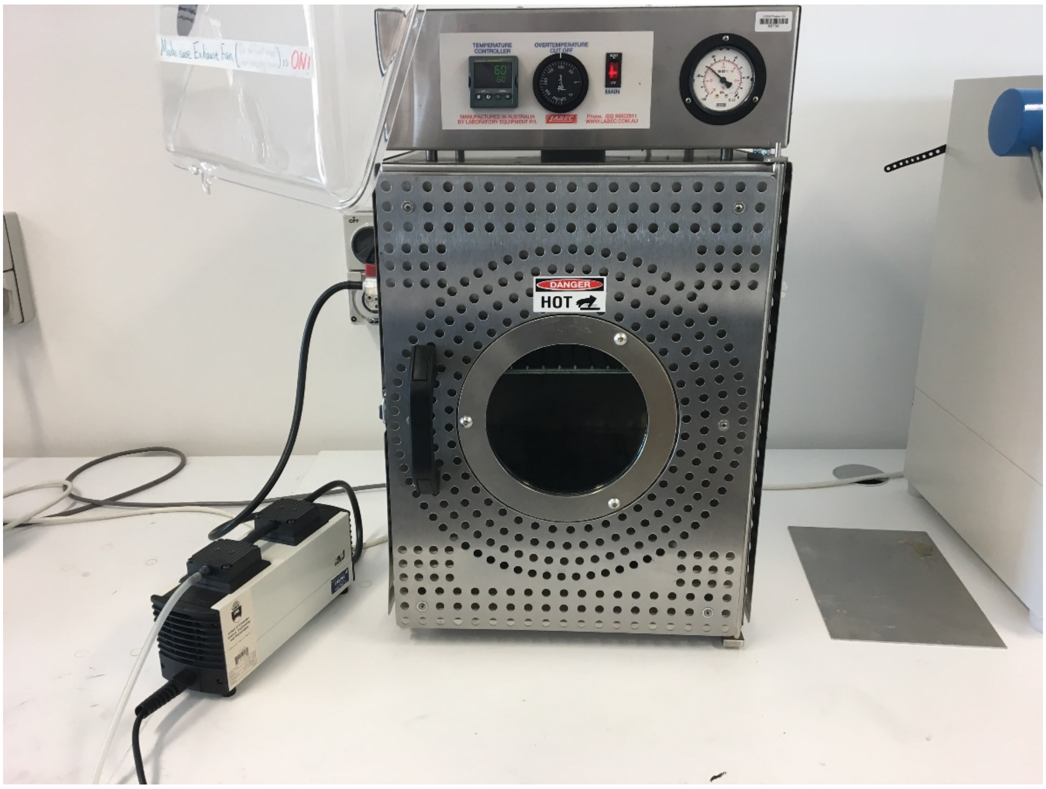

Figure A4: Laboratory Oven

The pump need to connect to a gas removal device. We used the organic solution to absorb the waste gas.

And temperature should be controlled based on the solution. For NMP dispersed graphene solution, the temperature should be set at 100° C. As for CNT conductive polymer solution, the temperature will be set at 60° C.

The pressure for this oven need to be -100 kPa to keep vacuum situation.

Support information for characterization

The strain test device is the Instron 5567 (Figure A5), which located at Tonsely level 3.

Figure A5: Instron vertical stretching machine

For this device, we need to combine with computer software to use it. The software is standard ASTM D412. The stretching speed should be 10 mm/s.

To test the resistivity at the same time, we combined the digital multimeter with computer. The digital multimeter is Agilent 34401a (Figure A6), which provided by mechanical service.

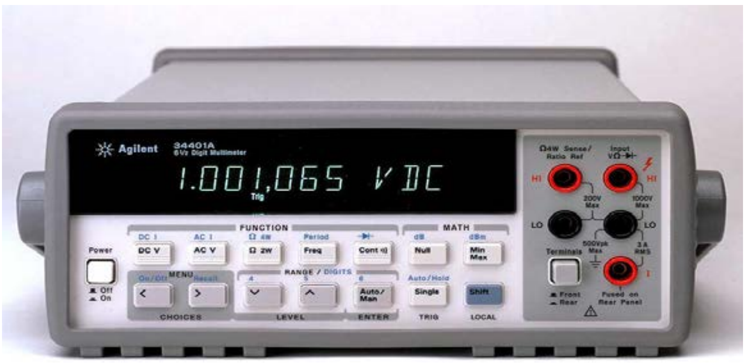

Figure A6: Agilent 34401a digital multimeter

And the software is the software, which made by the cooperation of our team and mechanical service. It is named 34401A DMM.

The SEM image (Figure A7) for the conductive rubber is shown as followed. Due to our experience and equipment situation, the images are not sufficient showing the microstructure. But it is shown that carbon nanotubes are not concentrated.

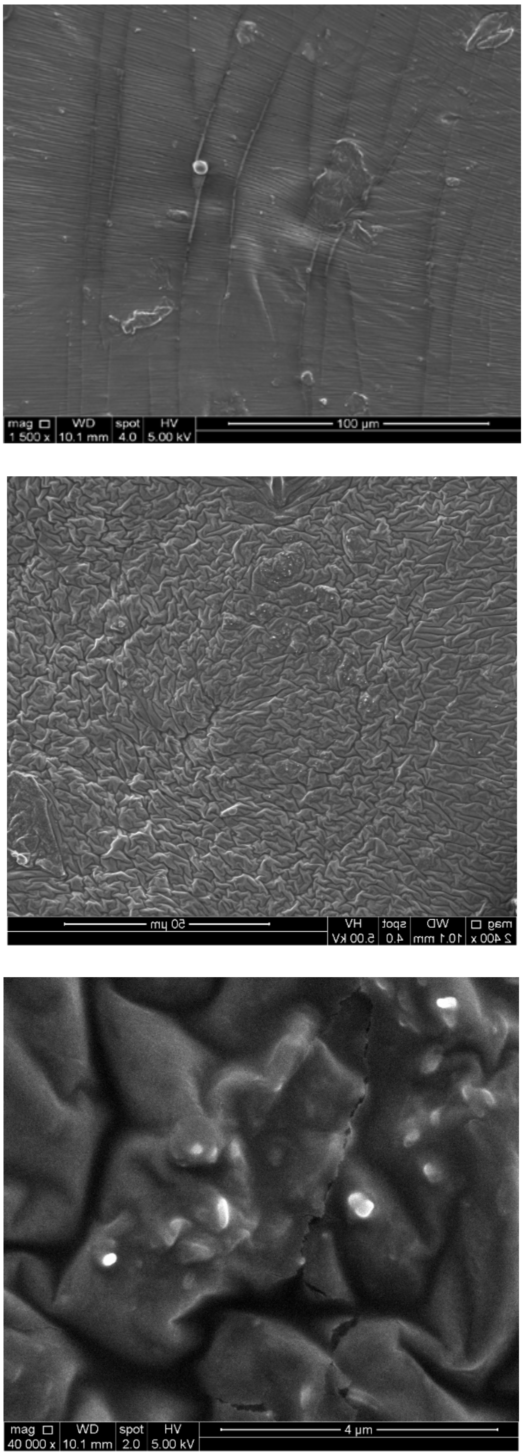

Figure A7: SEM images of CNT

(All relative data for the experiments were shown in the Chapter 3 & 4. The raw data will not be added into the thesis)

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