CERTIFICATION OF APPROVAL

EFFECT OF FUNCTIONALIZATION ON THE STRENGTH OF MULTI-WALL CARBON NANOTUBES-POLYPROPYLENE (MWCNTs-PP) COMPOSITE

By

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Approved:

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work obtained herein have not been undertaken or done by unspecified sources or persons.

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HOLINSON LEE

ABSTRACT

Carbon nanotube (CNT) has managed to capture the attention of many scientists world-wide. It is mainly because of the potential that it has to revolutionize many fields in the material science and nanotechnology areas [1]. With its small size and significant physical properties, it has become a very unique material. It also has a wide range of promising applications in various technological fields such as automobile, energy, medical, aerospace, chemical and etc. However, in recent years, scientists are having problems of utilizing the CNT's reinforcement potential into composites materials. Some example of the problem is the dispersion of CNT and also the load transfer from the matrix to CNT. In this project, there will be more focus given on the effectiveness of chemical functionalization using acid mixture and how it helps to improve the tensile strength of the MWCNTs-PP composite. The composite is produced using compression molding machine and the tensile test is conducted using the Universal Tensile Testing Machine. The result of the experiments shows that chemical functionalization helps to disperse the arrangement of the MWCNTs and also to remove the impurities present in the tubes to maximize the physical properties of the tubes. The MWCNTS in the polypropylene matrix also had proven to improve its tensile strength as composite reinforcement.

ACKNOWLEDGEMENT

Praise to God that I had managed to complete the two semesters of Final Year Project in Universiti Teknologi PETRONAS. Throughout the two semester period, many challenges had emerged and I want to thank all that has helped me to overcome all the challenges. Without all the helps, I would have not been able to complete this project.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Carbon nanotubes are some of the most outstanding new material to be ever discovered during the past 20 years [2]. Since their discovery, CNT have been predicted by scientists to have a huge potential to make the next generation composite material structure with much better physical and chemical properties [3]. CNT can be used to fulfill the demands of current and future technologies. The worldwide interest on CNT started when Sumio Iijima published a 1991 Nature paper [4]. Iijima was using a high resolution transmission electron microscope (HRTEM) in order to examine the carbons which are produced by the arc evaporation of graphite inside an atmosphere of helium [2]. It was while studying the deposits formed on the graphite cathode that he made his discovery which is that the central of the deposits formed contained a very large amount of small tubules of graphitic carbon.

After two years, Iijima and Ichihashi of NEC together with Bethune and colleagues in IBM Almaden Research Center managed to synthesize single-walled carbon nanotubes (SWCNTs) [4]. The SWCNTs were synthesized using the same method of synthesizing MWCNTs but with the addition of some metal particles into the carbon electrodes. SWCNTs can be differentiated from MWCNTs through its very small diameter (average ~1nm) and they are usually curled and looped rather than straight.

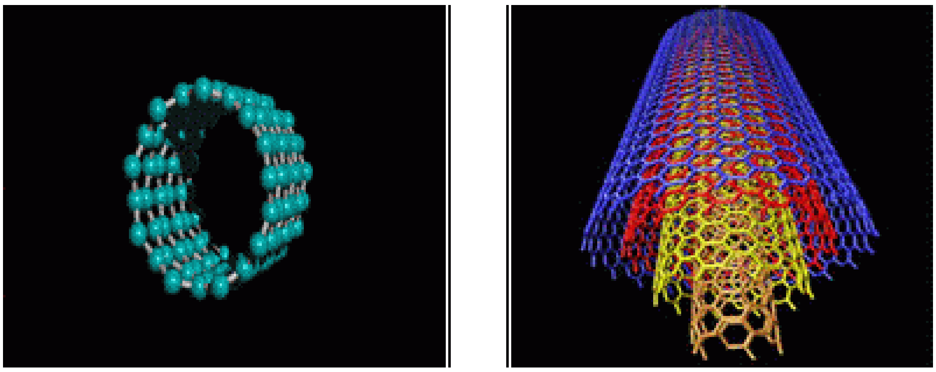

Fig. 1 The structure of SWCNTs (left side) and MWCNTs (right side) [5]

There are three methods that are commonly used to produce the CNTs namely are the arc discharge method, laser ablation method and the chemical vapor deposition method. Arc discharge method was the first SWCNTs and MWCNTs synthesizing technique that was recognized. This method uses two high purity graphite electrodes as the anode and cathode. The electrodes were then vaporized with DC current of 100 A running through the electrodes inside a helium atmosphere of 400 mbar. After a period of time, a carbon rod will built up at the cathode. The quantity and quality of the CNTs produced through this method varies depending on the parameters such as metal concentration, inert gas pressure, type of gas, temperature and etc.

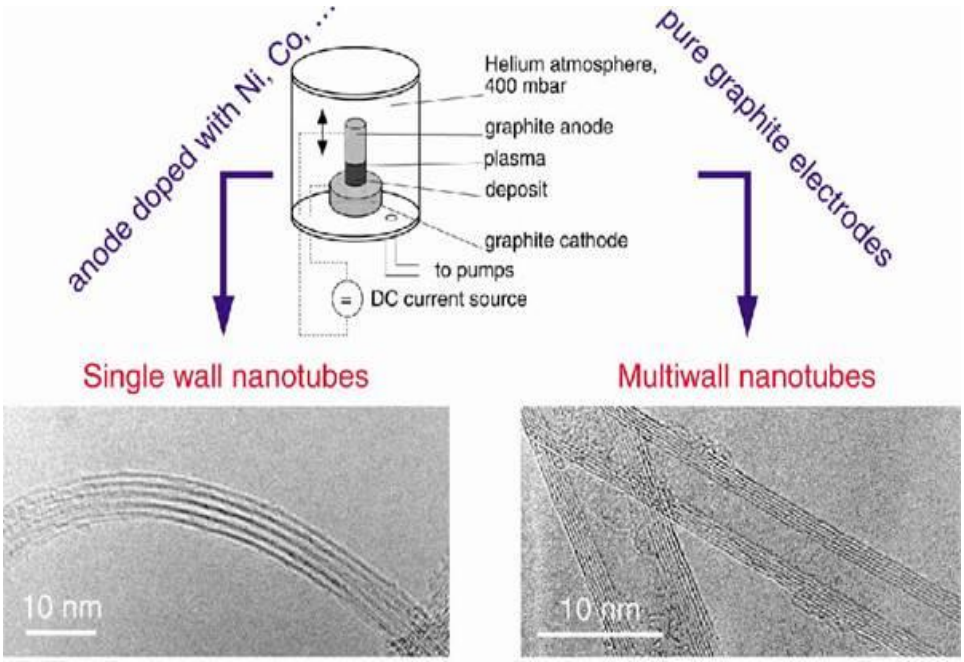

Fig. 2 Arc discharge method process [6]

The second method to synthesize CNTs is the laser ablation method. In this method, high power laser is used to vaporize the carbon from a graphite target at high temperature. The laser is focused onto a carbon target which contains 98.8% graphite and 1.2% cobalt inside a quartz tube furnace of 1200^{0}C with argon atmosphere of 500 Torr. The CNTs produced will self-assemble from the carbon vapor and then condensed on the wall of flow tube. CNTs produced through this method have very high purity up till 90% purity. The quality and quantity of the CNTs produced depends on the parameters such as type of catalyst, laser power, type of inert gas, temperature, pressure and etc.

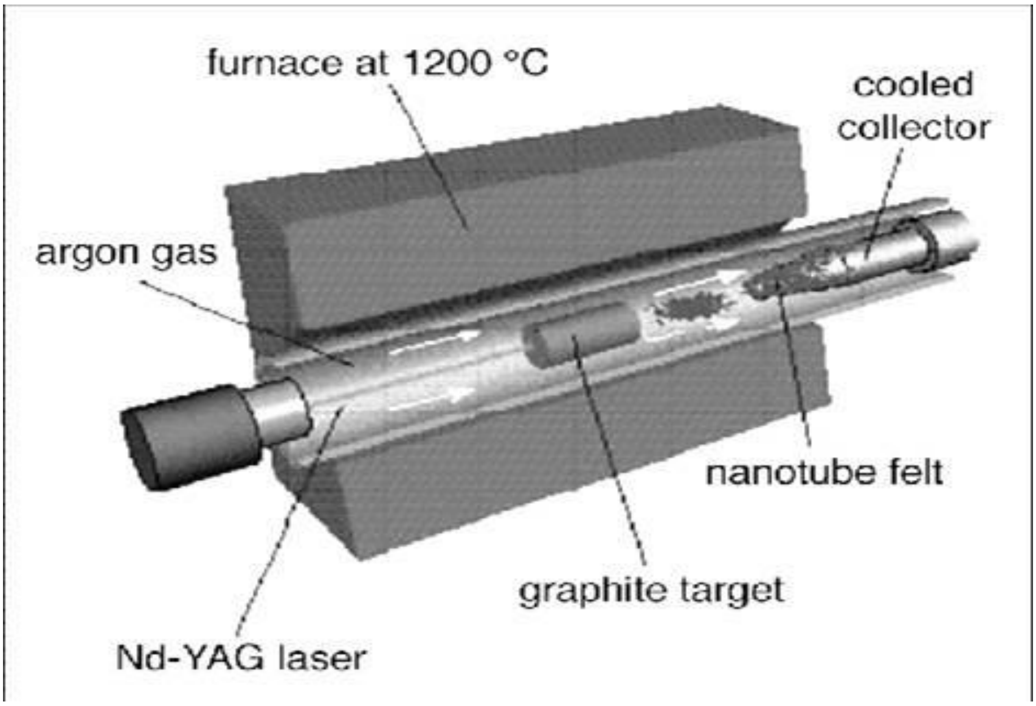

Fig. 3 Laser ablation method process [7]

The third method to synthesize CNTs is the chemical vapor deposition (CVD) method. This method can be achieved by taking a carbon source in the gas phase using an energy source like heated coil or plasma to transfer the energy to gaseous carbon molecules. This process uses hydrocarbons like carbon monoxide, acetylene and methane as the carbon sources. The hydrocarbons will be flowed through high temperature quartz tube at 720 ^{0}C. While at high temperature, the hydrocarbons will be broken down into pure carbon molecules and pure hydrogen molecules. Then the pure carbons will diffuse and bind at the substrate which is heated and coated with catalyst like Fe or Co. the advantage of CVD is the process required lower temperature range, can produce CNTs with high purity and low power input is required.

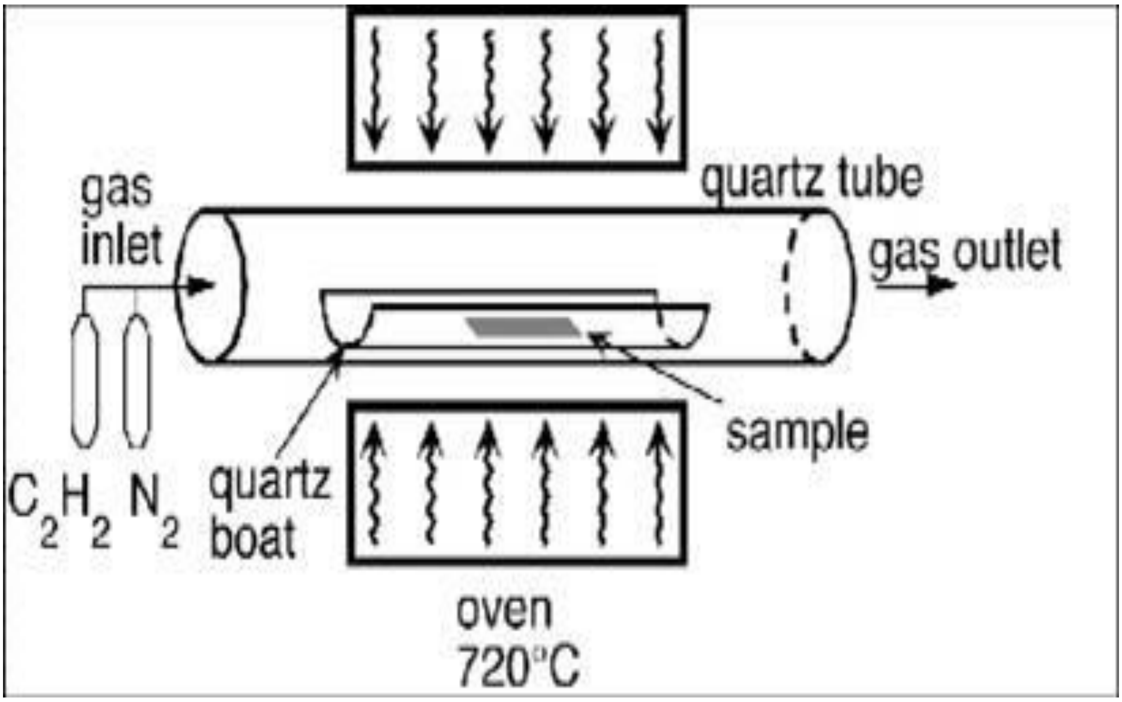

Fig. 4 Chemical vapor deposition (CVD) method process [8]

In a way, CNTs can be considered as a new form of pure carbon. Pure carbons have only two types of covalent bonds which are the sp^2 and sp^3 hybridization which dominate respectively in graphite and diamond.

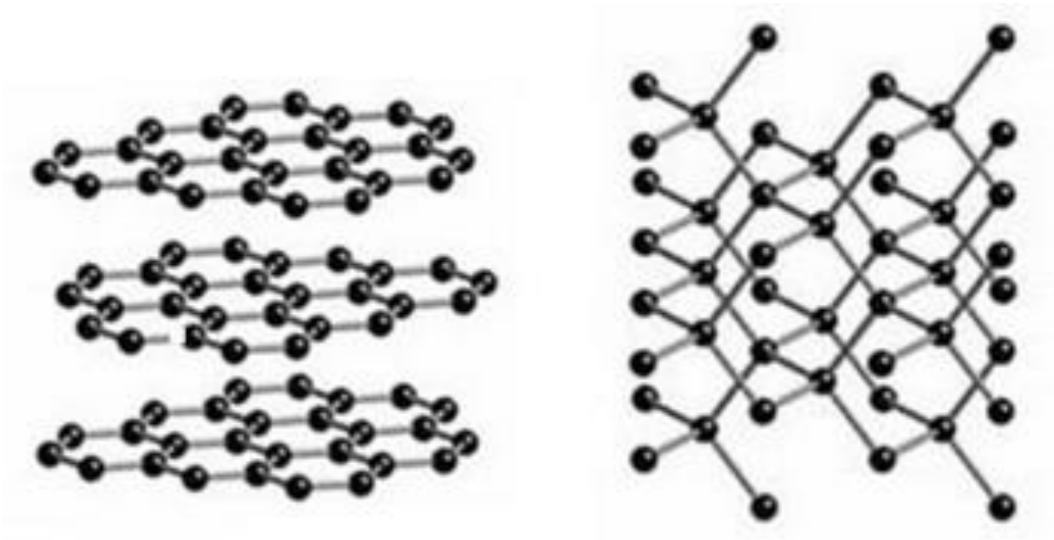

Fig. 5 The structure of graphite (left side) and diamond (right side) [9]

CNTs are macromolecules in cylindrical shape form with radius as small as a few nanometers but can be grown up till 20cm in length. The CNTs' walls are made up of hexagonal lattice of carbon atoms analogous to the atomic planes of graphite. They are capped between their ends by one half of fullerene like molecules.

Other than that, CNTs also possess many unique properties like chemical and thermal stability, high conductivity, extremely high tensile strength and elasticity and etc. It is proven that CNTs are the strongest fibers known today. Of the same weight with steel, SWCNTs can be up till 100 times stronger and higher Young’s Modulus of 1TPa, which is about 5 times greater than steel. Despite of the high strength and Young’s Modulus, CNTs has a low density of only 1.3 g/cm^3 and possess the thermal conductivity of about 2000 W/mK.

Some of the applications of CNTs are as the scanning probe tips. Due to the flexibility of CNTs, it is suitable to be used in scanning probe instruments. The flexibility of CNTs can prevent damage onto the sample surface and also the probe tip just in case the probe tips crash onto the surface. On the other hand, better image resolution can be obtained as to compare to the resolution obtained from using standard nanoprobes.

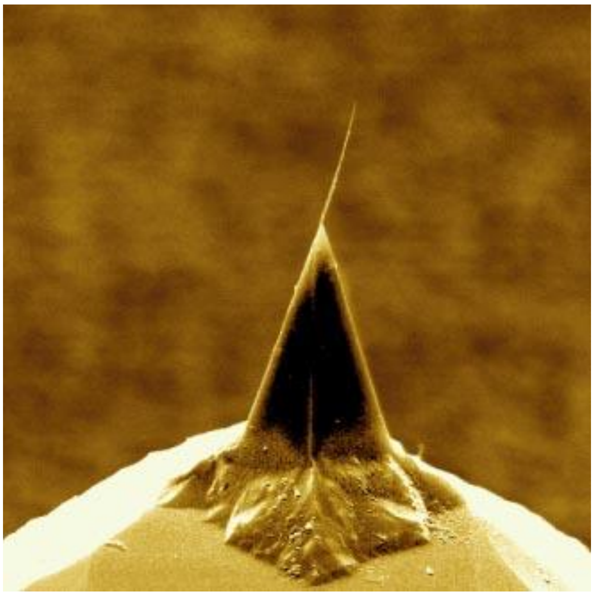

Fig. 6 Scanning probe tips [10]

1.2 Problem Statement

There had been many experiment results and research papers that show the advantages of CNT in terms of mechanical and chemical properties. But the best dispersion method for CNT is still being debated now. Each functionalization method has their own advantages and disadvantages respectively. But according to the literature done, chemical functionalization has much better result as compared to physical functionalization. In this study, chemical functionalization will be conducted onto the CNT and in the functionalization process; acid mixture will be used as the medium for sonication of the nanotubes. The best method of producing the MWCNTs-PP composite is also a problem that scientist still cannot answer. Thus, I will study the effects of chemical functionalization method to disperse the CNT and uses the compression molding method to produce the MWCNTs-PP composite samples and test the effect on strength of MWCNT/PP composite.

1.3 Objectives

1. To investigate the effectiveness of chemical functionalization in reducing agglomeration of MWCNT.
2. To assess the strength of MWCNT/PP composite with functionalized MWCNTs.

1.4 Scope of Study

In this study, high quality Multi-wall Carbon Nanotubes (MWCNTs) will be used as fiber reinforcement and polypropylene (PP) as the matrix for the composite. To functionalize the MWCNTs chemically, acid mixture that comprises of concentrated nitric acid and concentrated sulphuric acid with 3:1 ratio is used as the medium of sonication for the MWCNTs. The sonication time is 0.5 hour, 2.75 hours and 5 hours. To produce the MWCNTs composite, compression molding process will be used to produce the composite samples with different composition of MWCNTs according to weight percentage which are 0.5 wt%, 1 wt%, 2 wt% and 4 wt%. the composite samples will be produced according to the ASTM D638 I standard. Universal Tensile Testing Machine will be used for tensile testing of the composite sample.

CHAPTER 2
LITERATURE REVIEW

The study is focused on the effect of MWCNTs functionalization onto the tensile strength of MWCTs-PP composite. It is noted that the properties of MWCNTs are remarkable and a high quality MWCNTs will be used in this project to improve the dispersion and tensile strength of the composite produced. This literature review is made based on the references from 20 papers.

2.1 Multi-Wall Carbon Nanotubes (MWCNTs)

The uniqueness of carbon nanotubes came from the structure. According to P.M. Ajayan, this is because of the helicity in the arrangement of the carbon atoms in hexagonal arrays which produces the surface honeycomb lattices [11]. The electronic density changes significantly because of the helicity and tiny diameter, and hence possesses a unique electronic characteristic [11]. These characteristics had created a new range of electronic device applications.

Another important factor that makes carbon nanotubes' physical attributes very unique is the topology or the nature of the individual nanotubes shells. When the individual layers are arranged close to each other, some of the anisotropic properties of graphite disappear which makes it completely different from graphite. With the combinations of size, structure and topology of carbon nanotubes, they are able to have a very good physical attributes such as high stability, stiffness and strength.

Mainly, there are 2 types of carbon nanotubes that can have high structural perfection which are the single-walled nanotubes (SWNT) and the multiwall nanotubes (MWNT). Single-walled nanotubes consist of single graphite sheet which is seamlessly wrapped until it forms a cylindrical tube. Multiwall nanotubes comprises of layers of nanotubes which are concentrically nested to be just like the ring of the tree trunk.

In current world technology, there are high demands for materials that are stronger, lighter and possess a high level of flexibility and capacity. Based on R. Khare's finding, we can expect the carbon nanotubes to have high stiffness and axial strength due to the carbon-carbon sp^2 bonding that they have [1]. There are a lot of experimental and theoretical studies done on carbon nanotubes properties and J.N. Coleman suggest that they are known as the stiffest fiber known until today, with expected Young's modulus of as high as 1 TPa [2]. Other than that, carbon nanotubes are also known to have elongation to failure of 20-30% [1]. With the Young's modulus combined with the elongation to failure, S.Kumar found that carbon nanotubes can have tensile strength as high as 1.72 GPa and tensile modulus of 450 GPa [12]. If we compare with high-strength steel, carbon nanotubes certainly have better mechanical properties because high-strength steel has Young's modulus of only around 200 GPa and tensile strength of only 1-2 GPa. Not only that, since carbon nanotubes are lighter than high-strength steel, it is obvious that carbon nanotubes are a much better choice as compared to high-strength steel in terms of physical properties.

Before scientists discovered CNT along with its attributes, diamond was the best thermal conductor around [1]. Recent experimental studies by R. Khare on CNT show that it has at least twice of the thermal conductivity of diamond [1]. J. Xiong also mentioned that CNT is known to be able to improve the thermal stability and conductivity of composites [13]. CNT can also be used to make anisotropic composites due to their great thermal, electrical and magnetic properties [13]. CNT can have thermal conductivity of up to 12 MW/mK and it's due to the high-frequency phononic conduction modes in CNTs [14]. Some other experiments suggest that the thermal conductivity of CNT is lower which is between 20 till 6000 W/mK depending on the CNT preparation methods [15].

The significant electrical property that CNT has is mainly due to its peculiar electronic structure of graphite and its 1-D character [1]. Not only has that, the inter-tube contacts of CNT allowing it to have excellent conductivity because it is easier for electron to transfer between tubes [1]. Stretched CNT has a much better electrical conductivity as to compared to unstretched CNT which contains a lot of waviness [1]. CNT in composite can increase the conductivity of the material up till 32% [16].

2.2 Functionalization of Multi-Wall Carbon Nanotubes (MWCNTs)

The functionalization for CNTs can be divided into two types which are physical and chemical functionalization [17,18]. One of the examples of physical functionalization method for CNTs is by using surfactant [19]. Surfactants can be absorbed by the CNTs very easily and make them to be soluble in aqueous and organic solvents [20]. After the surfactant is absorbed into the surface of CNTs, the self-organization of the surfactant into micelles can be expected to occur above critical micelle concentration (CMC) [21]. An example of surfactant is Sodium dodecylbenzenesulfonate (NaDDBS). Based on S.H. Lee, he suggest that the size of aggregate of MWCNTs can be greatly reduced and achieve uniform dispersion by adding compactilizer [22]. This can greatly enhanced the result of physical functionalization using NaDDBS to disperse the MWCNTs.

In the case of chemical functionalization of CNTs, one of its examples is by using solution of nitric and sulphuric acid because they are known to be the most effective in modifying the CNT surface and change the formation of its functional group [23]. One other example of chemical functionalization method is by using the silane coupling agents which can help to increase the interfacial adhesion between the CNTs and polymer [24]. According to the findings by P. Guo in his experiments, he mentioned that chemically functionalized MWCNTs using aqueous acids can help to make the surface of MWCNT to get attached polar functionalized groups like –C-O and –OH which can help to improve MWCNTs/polymer interfacial interaction [25].

2.3 Polypropylene (PP)

Polypropylene (PP) is basically a plastic polymer or also known with its chemical formula of C3H6. PP is widely used both in industrial work and consumer goods. It can also be used as either fiber or structural plastic. Some example of structural plastic application is the food containers which we use in our everyday life.

PP resins falls under the general class of thermoplastics which is produced from the propylene gas. We can get propylene gas from the cracking of natural gas feed stocks or as the petroleum by-products. If processed under different temperature and pressure, propylene can polymerizes and form very long polymer chains [26].

Based on “Characteristics & Benefits of Polypropylene” by C&E Plastics Inc, polypropylene is easily machined and cut, they are lightweight and rigid and also has excellent thermal insulating properties. They also mentioned that polypropylene has excellent dielectric properties, low moisture absorption, high tensile strength and high chemical and corrosion resistance. Not only that, polypropylene also have a long life span, has excellent abrasion resistance and easy to maintain and clean [26].

C&E Plastics Inc also suggest that, as to compare with other existing thermo-forming and polyolefin materials, polypropylene has better quality, more versatile and cost effective plastic. Not only it has good surface hardness and impact strength, but it also has excellent abrasion resistance and dimensional stability. PP is also known to be resistance towards a wide range or acids, alkalis and solvent solutions with the temperature range up to 200^0F [26].

PP is a homogeneous material which possesses same corrosion resistance attributes throughout. This means that PP does not need additional maintenance like re-coating inside and out to guard against corrosion. PP can be found commonly in natural, grey and black colours. PP with black and grey pigments has much better UV qualities which can be apply for outside use. PP can also be found in flame retardant grade [26].

Many are interested to use nanoscale reinforcing fillers to make polymeric nanocomposite materials with greater properties like CNT-Polypropylene composite [25]. CNT can help to increase the yield strength of the nanocomposite and also reduce its ductility [22,26]. Not only that, the electrical conductivity of the composite will increase with the presence of CNTs as the reinforce fibres [26]. Other than that, CNTs are also known for their remarkably high thermal conductivity and also high density [25].

2.4 MWCNTs-PP Composite Tensile Strength

According to the paper by M.Awang and et. [27], same chemical functionalization method is used for the MWCNTs treatment and same acid mixture is used. Below is the result of tensiel strength testing of the MWCNTs-PP composites produced [27]:

Table 1. Tensile Test Result [27]

Sample	Low Quality MWCNTs	
	Tensile Strength (MPa)	Percentage Increase (%)
PP	28.96	-
PP + 0.5wt% Pure MWCNTs	30.31	4.64
PP + 1wt% Pure MWCNTs	32.47	12.11
PP + 2wt% Pure MWCNTs	33.32	15.04
PP + 4wt% Pure MWCNTs	32.56	12.42
PP + 0.5wt% Functionalized MWCNTs	30.83	6.45
PP + 1wt% Functionalized MWCNTs	32.90	13.59
PP + 2wt% Functionalized MWCNTs	33.63	16.09
PP + 4wt% Functionalized MWCNTs	33.98	17.32

The result of tensile testing from the MWCNTs-PP composite that is produced later will be compared with the tensile testing result above. This is aimed to determine which experiment manages to produce MWCNTs-PP composite with the best tensile strength.

CHAPTER 3

METHODOLOGY

3.1 Project Workflow

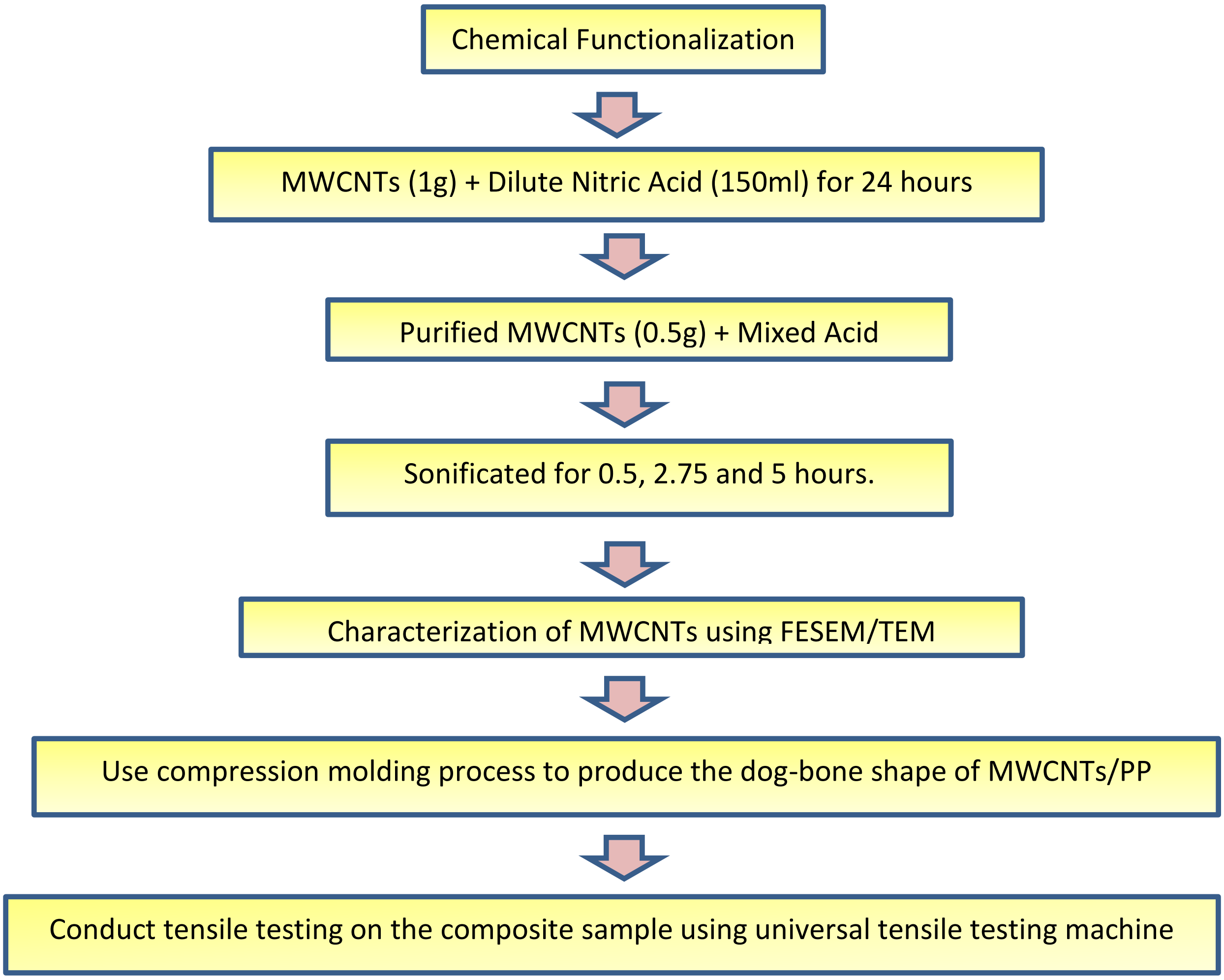

Figure 7. Project Methodology

3.1.1 Functionalization of High Quality MWCNTs

For the chemical functionalization process, one gram of high quality MWCNTs will be purified by using 150ml of diluted nitric acid (20 wt%) for 24 hours in a water bath at room temperature (28 ^{0}C). This process aims to remove the impurities present in the MWCNTs like unwanted amorphous carbon and also metal catalyst. After that, 0.5g of the purified MWCNTs will be chemically modified with the help of mixed acids and then sonicated together for 0.5 hours, 2.45 hours and 5 hours at room temperature (28 ^{0}C) at constant power output of 140 W. The mixed acids include concentrated nitric acid (67%) and concentrated sulphur acid (98%) with the volume fraction of 1:3. After the sonification process, the acid-treated MWCNTs will be washed with distilled water until its reach pH 7 and then dried inside a vacuum oven at 80 ^{0}C. Thus, the MWCNTs are ready for experiments and be mixed with PP to produce the composite.

3.1.2 Characterization Study of Functionalized High Quality MWCNTs

The experiments that will be conducted onto the specimens are the Scanning Electron Microscope (SEM) and Transmission Electron Microscopy (TEM) to produce image of material up to nano level. SEM images will be taken at the magnifications of 50K only because we need only need the images of the dispersion of bulk nano tubes. TEM images will be taken at the magnification of 80K and 200K to detect the presence of impurities inside the nano tubes. With the help of SEM or TEM, we can study the arrangement of the MWCNTs before and after they are functionalized using chemical treatment. Thus, we can find out whether chmical functinalization method is effective in order to purify and get the maximum dispersion arrangement of the MWCNTs.

3.1.3 Fabrication of MWCNTs-PP Composite Samples

Due to the unavailability of both melt mixing machine and injection moulding machine in the campus, this project will resolute to the compression moulding to fabricate the MWCNTs-PP composite samples. After the composite pallets are produced by mixing the melted PP with MWCNTs and grinded them, they will be shaped according to the shape of the "dog-bone" which are commonly used in the polymer tensile test. The composite sample will be produced according to

ASTM D638 I standard. The pallets will be put into a mould which resembles the ASTM D638 I standard, it is put into the compression moulding under the temperature of 220 ^{o}C and pressure of 800 bar for 30 minutes. Then the mould will be allowed to cool down before removing the samples from the mould. There will be 7 sets of samples with different weight percentage of MWCNTs in the composite. Namely are pure PP (0 wt%), 1% of MWCNTs (1 wt%), 2% of MWCNTs (2 wt%), 4% of MWCNTs (4 wt%), 1% of functionalized MWCNTs (1 wt%), 2% of functionalized MWCNTs (2 wt%) and 4% of functionalized MWCNTs (4 wt%).

3.1.4 Tensile Test for MWCNTs/PP Composite

For the specimen of MWCNT/PP composite, polymer tensile test will be conducted onto it to determine the tensile strength of the composite sample. The sample will be placed in the grips of the universal tester and pulled until failure is reached. An extensometer will be used to determine the elongation and tensile modulus of the sample. The results that we can onbtained from the test is the sample's Young's modulus. Then the result will be compared to the findings from other experiments done by other people.

3.2 Gantt Chart

Table 2. Project Gantt Chart

Item/Week	FYP 1														FYP 2													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Literature Review																												
Procurement																												
Preparation of Surfactant solution and sonification process																												
Preparation of chemical solution and sonification process																												
Characterization of Functionalized MWCNTs Using SEM/TEM																												
Fabricate MWCNT/PP Composite Sample Using Injection Molding																												
Tensile Testing on Composite Sample																												
Thesis Write-up																												

Project Development

Key Milestone

3.3 Key Milestone

Table 3. Key Milestone

Milestone	Due Week
Completion of Procurement Process	2/8/2013 (Week 11 - FYP 1)
Completion of Study on Functionalized MWCNTs Using SEM/TEM	1/11/2013 (Week 6 - FYP 2)
Completion of Tensile Testing on Composite Sample	29/11/2013 (Week 10 - FYP 2)
Completion of Thesis Write-up	27/12/2013 (Week 14 - FYP 2)

CHAPTER 4

RESULT AND DISCUSSION

4.1 Purification of MWCNTs

After going through ultrasonication process in acid mixture for 2.75 hours, the Multi Wall Carbon Nanotubes (MWCNTs) are sent for testing using Transmission Electron Microscope (TEM). The reason why MWCNTs that are sonicated for 2.75 hours instead of those sonicated for 0.5 hour and 5 hours is because the optimum time for sonication of MWCNTs is about the hours. The acid mixture might not able to properly clear the nano tubes for the 0.5 hour sonication time because of time constraint. On the other hand, for the 5 hours sonicated MWCNTs, the nano tubes are damaged under prolonged acid treatment. This causes the nano tubes to become very short and dispersed.

The TEM model used is the Zeiss Libra 200 under the magnification of 80Kand 200K. TEM took the image of both the pure MWCNTs and also functionalized MWCNTS to compare the purity of the tubes. From the images, we can compare the presence of impurities in the nano tubes. The images taken are shown below;

As we can observe, there are presence of black dots inside the tubes. This shows that there are some impurities presences in the tube. Those impurities might be the residual catalyst that is not removed properly after the formation of the MWCNTs. These impurities can make the MWCNTs to lose or degrade their remarkable properties because impurities can prevent the matrix to enter the tubes properly. This can cause the MWCNTs to not be covered fully by the matrix inside out and reduce its tensile strength due to the ineffective distribution of forces from the matrix.

From the observation of the TEM images, it shows that the number of black dots in the image have decreases a lot. This can be explained by going back to the sonication process. When the MWCNTs are being sonicated, the acid mixture is allowed to flow into and through the nano tubes. After that, the catalyst is either reacted with the acid or washed away together with the acid and leaving empty hollow nano tubes.

If the two observations are compared to each other, we can conclude that the MWCNTs that is functionalized for 2.75 hours has lesser impurities over the pure MWCNTs. This also means that 2.75 hours functionalized MWCNTs is more suitable to be used as reinforcement in the MWCNTs-PP composite because there will be less impurities that can affect its tensile strength. This can promise a much better stress transfer from the matrix, in this case is PP, to the MWCNTs.

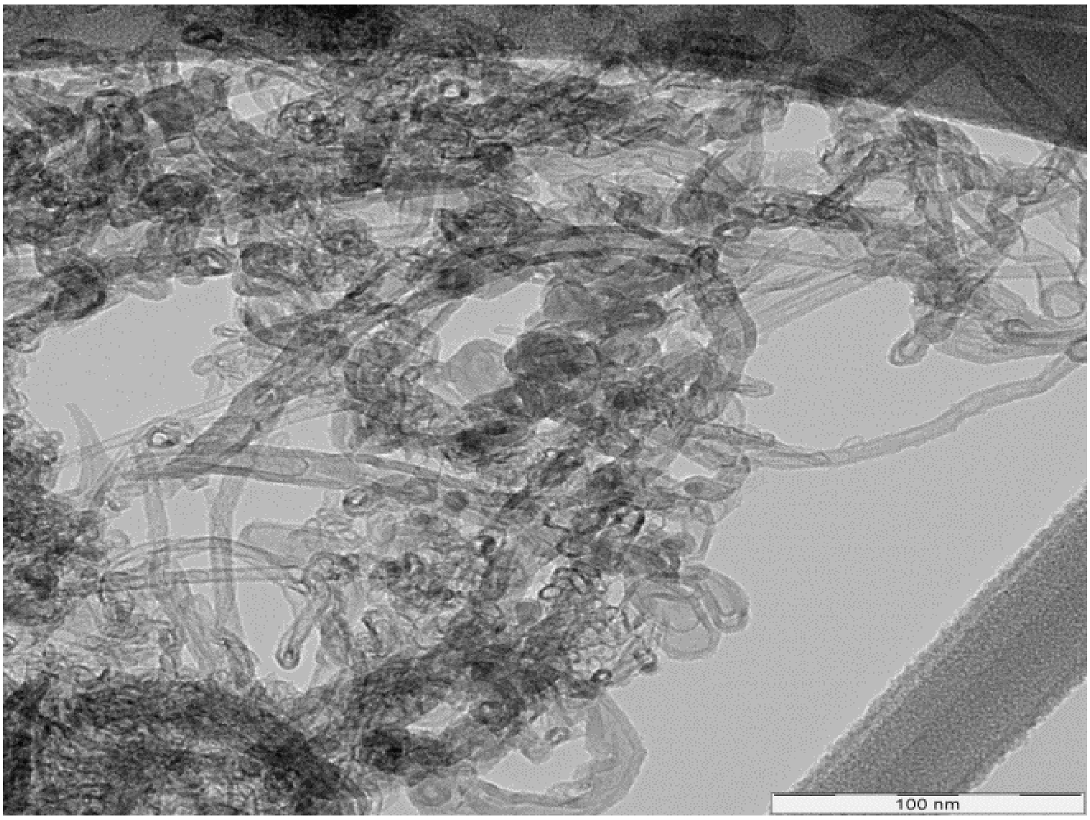

Fig 8. TEM Image of Original High Quality MWCNTs (80K)

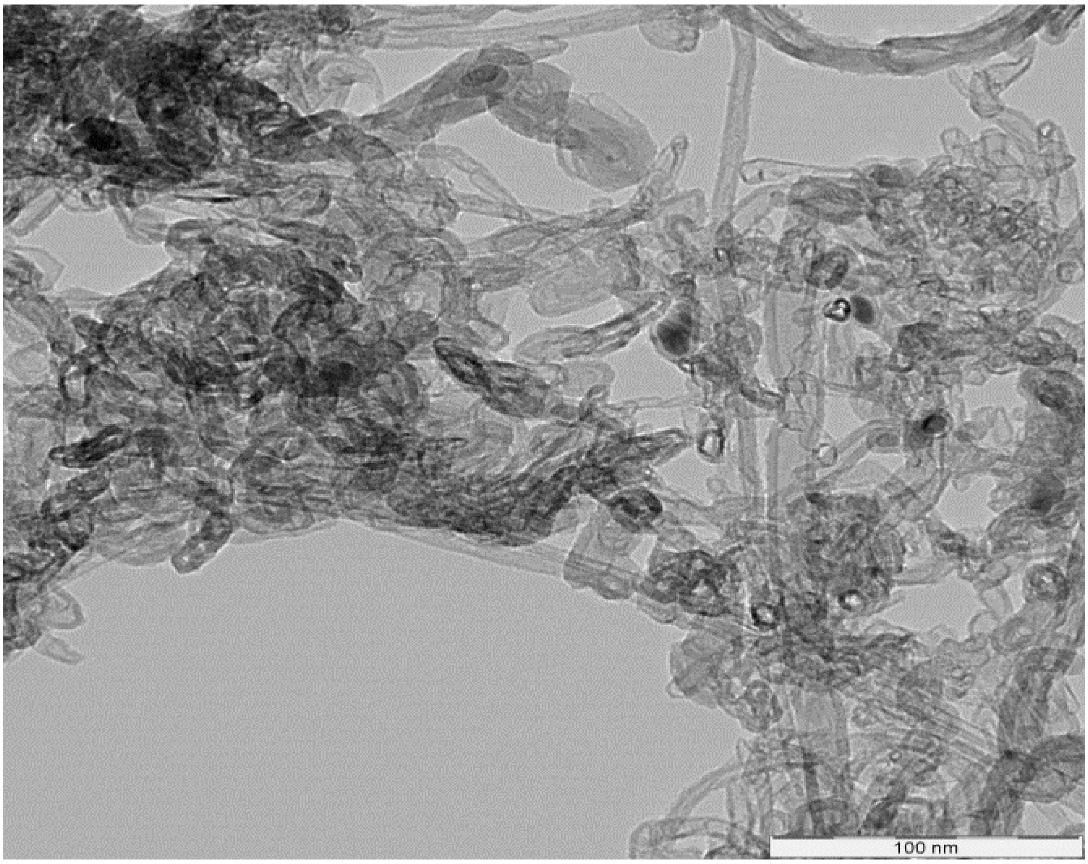

Fig 9. TEM Image of Original High Quality MWCNTs (200K)

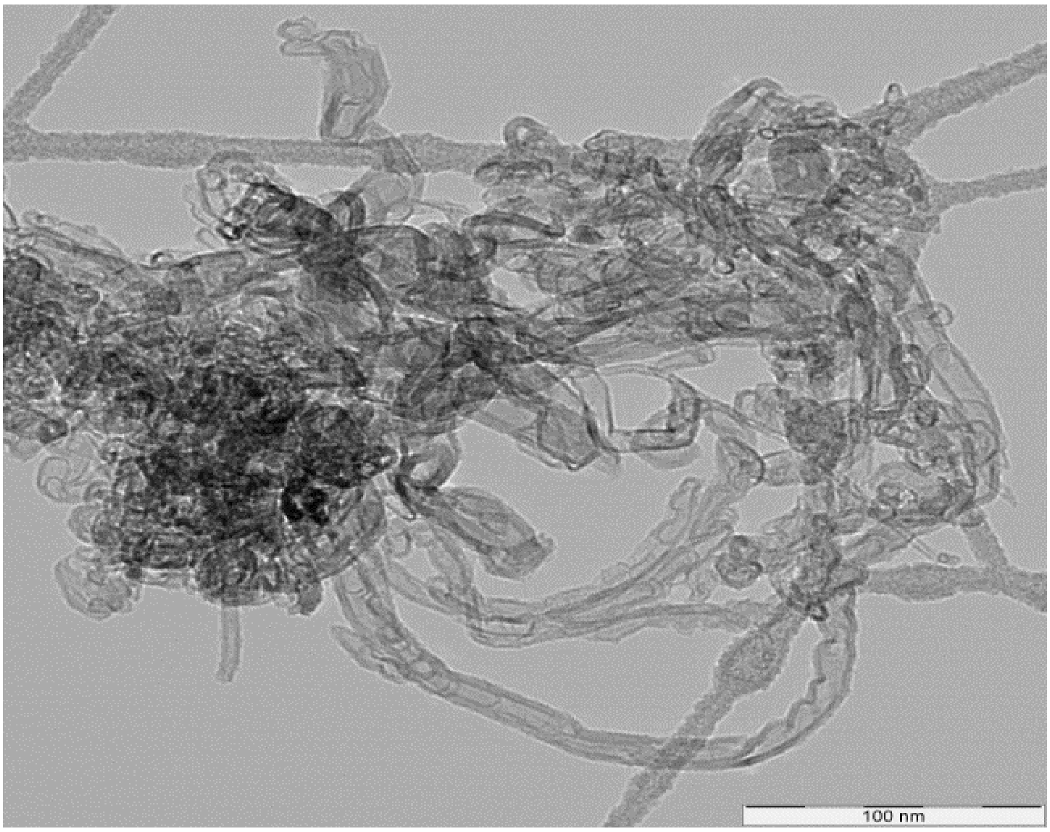

Fig 10. TEM Images of Functionalized MWCNTs (80K)

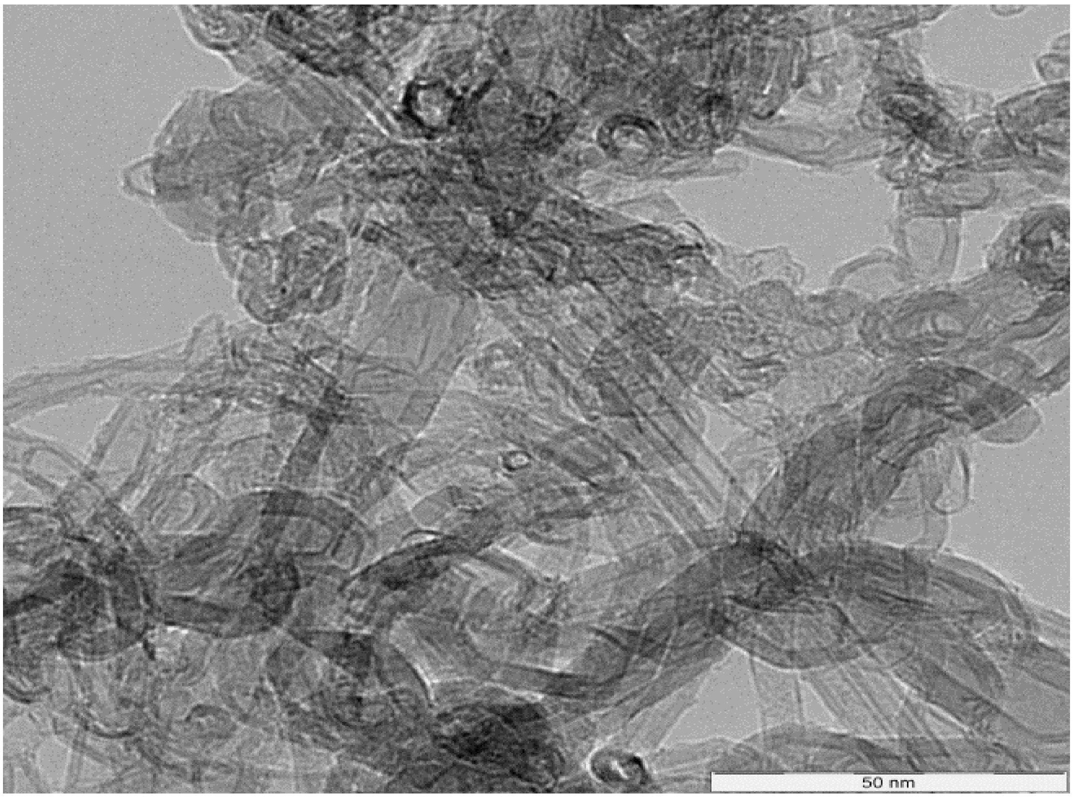

Fig 11. TEM Image of Functionalized MWCNTs (200K)

4.2 Dispersion of MWCNTs

After the functionalization process is done, the MWCNTs went through characterization process by using Field Emission Scanning Electron Microscope (FESEM) to determine their dispersion arrangement before and after functionalization process. The FESEM machine model used is FESEM Zeis Supra 55VP. Since only the arrangement of MWCNTs needed to be determined, so only 10K and 50K magnification is used to capture the image of the tubes.

Unlike the TEM characterization process, all 4 samples will be scanned using FESEM to compare which sample has the best dispersion arrangement. The 4 samples are namely the original high quality MWCNTs, functionalized MWCNTs for 0.5 hour, functionalized MWCNTs for 2.75 hours and functionalized MWCNTs for 5 hours.

As we can observe from figure 11, the MWCNTS are clumping with each other as they had not undergone any functionalization process. Even from the magnification of 10K, it is obvious that clumps or balls of MWCNTs tangled together. If this sample is used to produce the MWCNTs-PP composite, it might not able to perform to its full ability. The clumps of MWCNTs will present not as reinforcement but as impurities and reduce the tensile strength of the composite samples.

When we compare the condition of the MWCNTs in figure 11 and figure 12, the MWCNTs in figure 12 is more obvious and has more dispersed arrangement unlike the MWCNTs in figure 11 which has big clumps of MWCNTs. Although the MWCNTs had only gone through half hour of sonication time inside mix acid solution, obvious changes can already be seen that the MWCNTs has more dispersed arrangement. Despite of the changes, the functionalized MWCNTs for half hour is still not suitable to be used into making the MWCNTs-PP composite because the clumps of MWCNTs still present among the tubes. This might have better performance as reinforcement as to compare with the original MWCNTs but still not very effective as what we can hope for from MWCNTs. This has proved that chemical functionalization is effective is helping to disperse the arrangement of MWCNTs by using acid mixture but certainly half hour is not enough to make the MWCNTs to disperse properly in the acid.

As for figure 13, very obvious strands of MWCNTs can be seen throughout the image. There are also gaps between the MWCNTs which show that they are not clumping together as a single mass. To compare with figure 11, the functionalized MWCNTs for 2.75 hours has a much better dispersion arrangement among the tubes and very little number of clumps can be seen in the image unlike the original MWCNTs which has many clumps of MWCNTs.

When we compare figure 12 and figure 13, although the functionalized MWCNTs for half hour has become more dispersed after the process, but the functionalized MWCNTs for 2.75 hours has better dispersion arrangement. There are also lesser clumps of MWCNTs presence in figure 13 as compared to figure 12. This means that the functionalized MWCNTs for 2.75 hours are much better as compared to functionalized MWCNTs for half hour in terms of the dispersion arrangement of the tubes.

As for figure 14, the MWCNTs had been functionalized for 5 hours in acid mixture and the tubes are very dispersed as compared to the previous three images. As comparison to figure 11 and figure 12, the MWCNTs in figure 14 is more dispersed in terms of arrangement. This proves that the MWCNTs that is functionalized for 5 hours is much better to be used into MWCNTs-PP composite rather than the original MWNCTs and the functionalized MWCNTs for half hour. This is because the MWCNTs in figure 14 has better chance of providing more efficient load transfer from the matrix to the tubes because the tubes can be coated more with PP matrix.

On the other hand, when we compare the MWCNTs functionalized for 2.75 hours and MWCNTs functionalized for 5 hours, the MWCNTs functionalized for 2.75 hours seems to have the upper hand. Although the MWCNTs in figure 14 is much more dispersed as compared to the MWCNTs in figure 13, but the tubes in figure 14 is not very obvious like the tubes in figure 13. This is because of the usage of the acid mixture which mixes two concentrated acid (concentrated sulphuric acid and concentrated nitric acid). When the tubes is exposed to the acid mixture for long period of time, the acid can harm the tubes and broken it down into several parts.

That is why the MWCNTs in figure 14 are not very obvious like in the figure 13. The tubes has already been damaged and broken into several parts which make the tubes to become shorter and less obvious when using 50k magnification in FESEM. The MWCNTs that are too short is not very suitable to be used as reinforcement because the length of the tubes also affects the load transfer from the matrix to the tube. Longer tubes can act as better reinforcement as compared to shorter tubes.

Thus, when we compare all four images of different MWCNTs, it is clear that the MWCNTs functionalized for 2.75 hours is the best choice of MWCNTs to be used in making the MWCNTs-PP composite because it has dispersed arrangement of tubes but still retains its long length tubes which can help in making it a strong reinforcement.

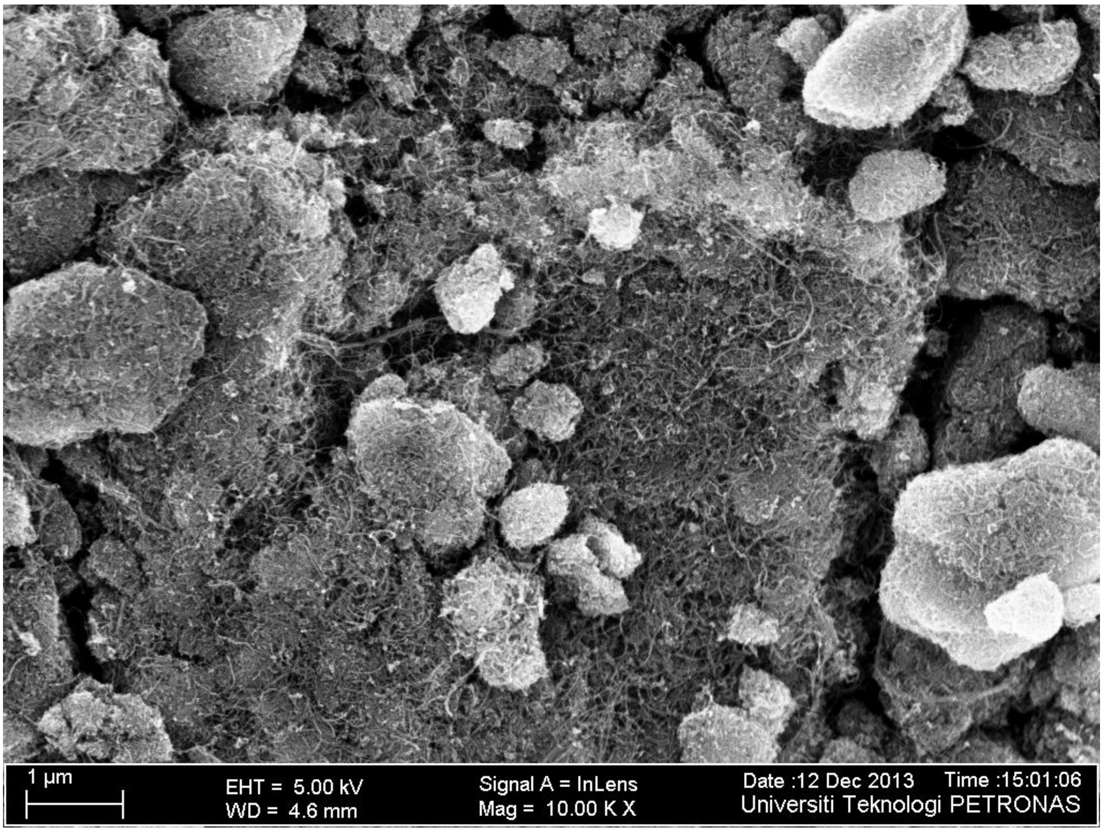

Fig 12. FESEM Image of Original High Quality MWCNTs

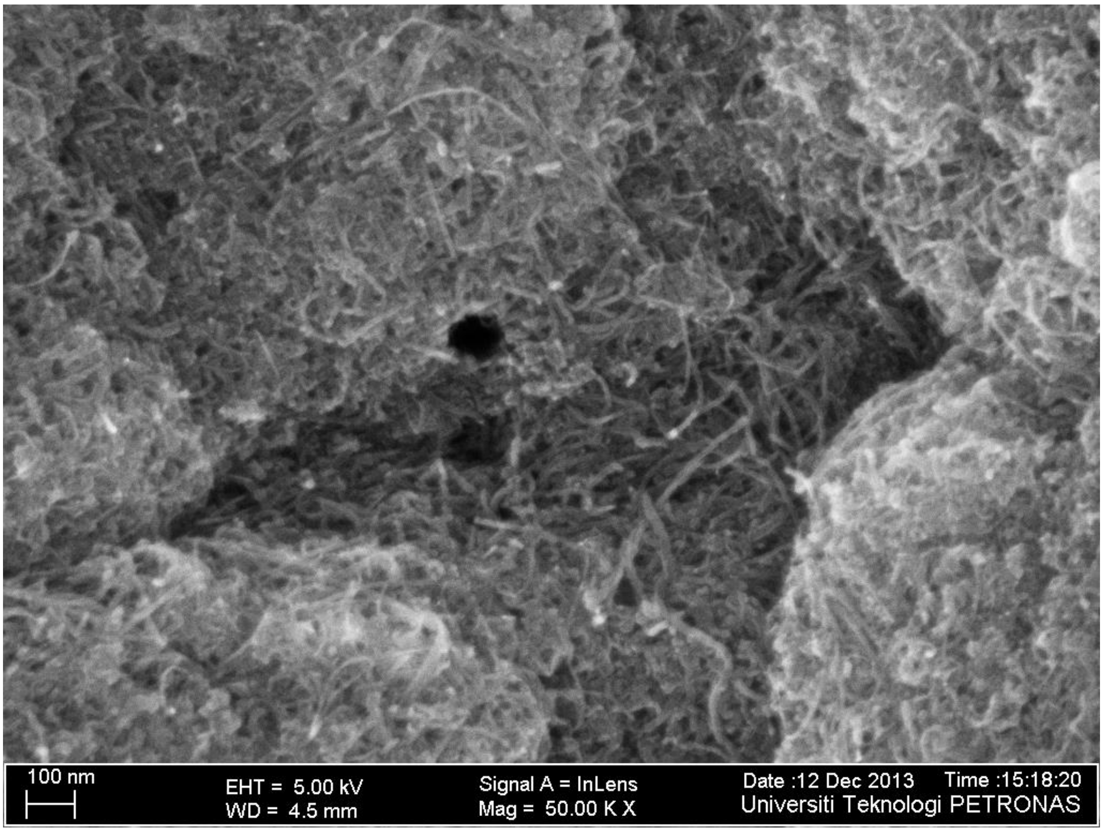

Fig 13. FESEM Image of Functionalized MWCNTs for 0.5 hour

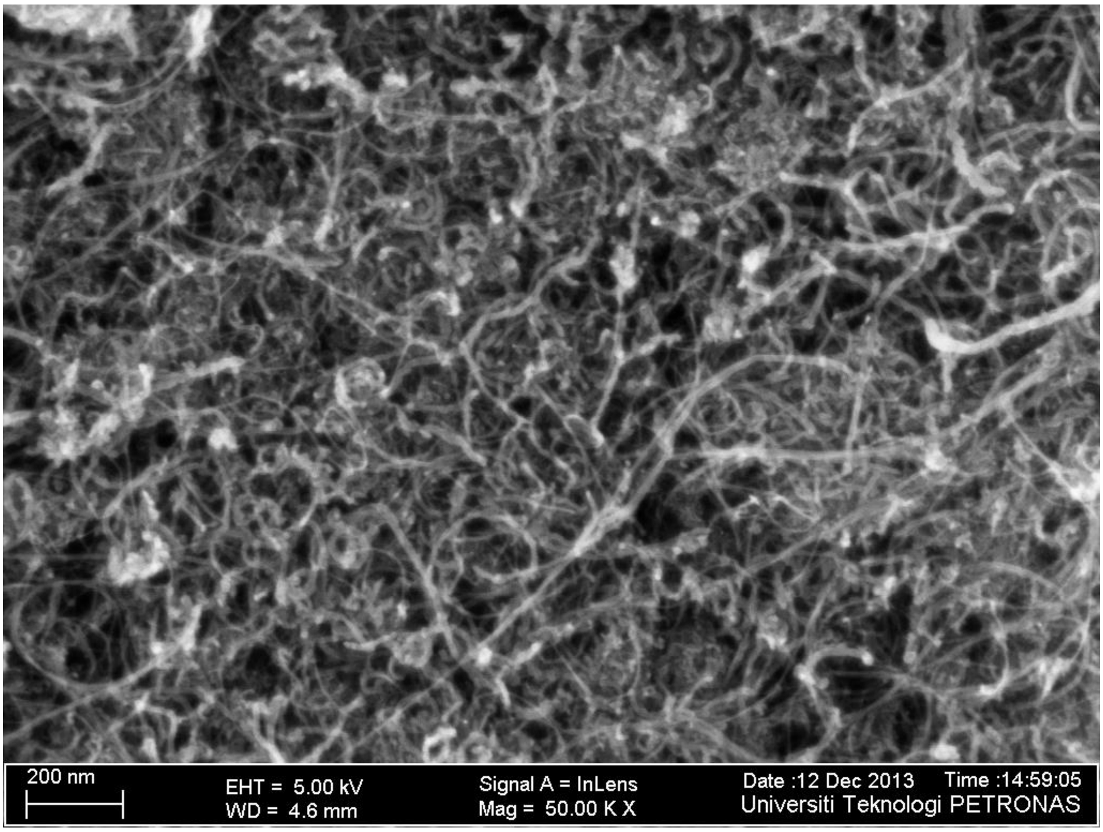

Fig 14. FESEM Image of Functionalized MWCNTs for 2.75 hours

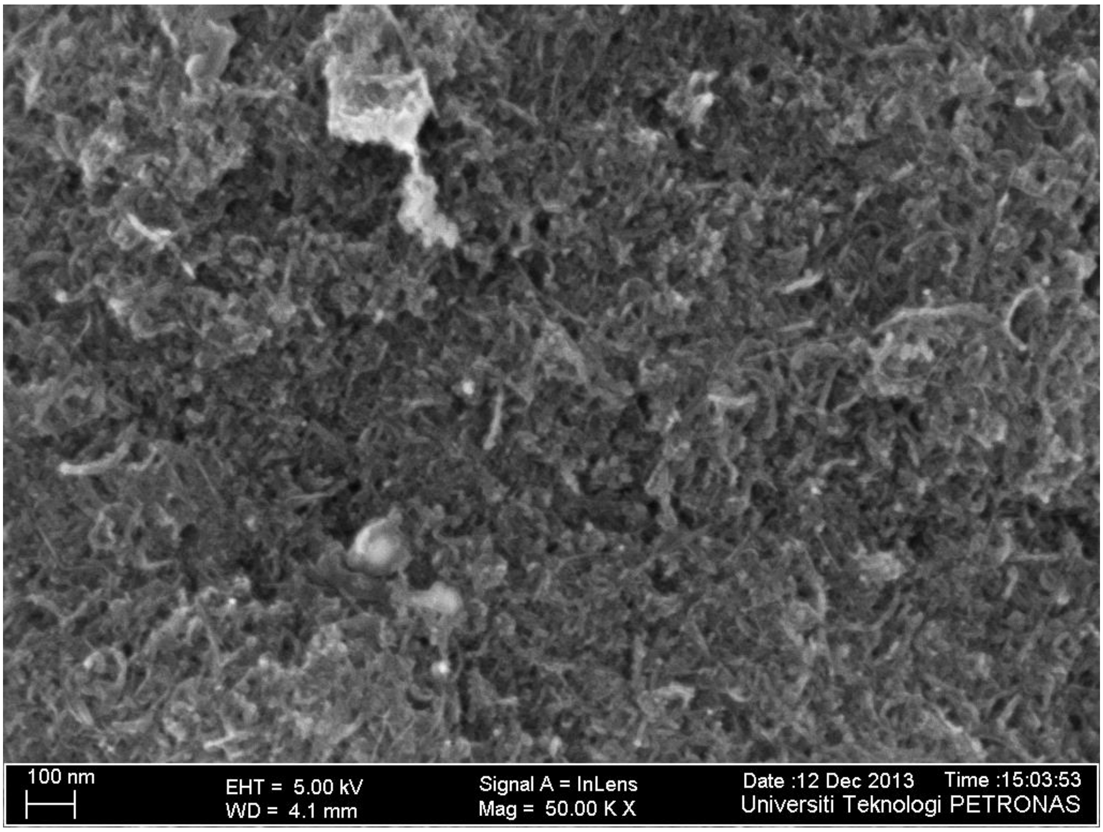

Fig 15. FESEM Image of Functionalized MWCNTs for 5 hours

4.3 Tensile Strength of MWCNTs-PP Composite

For this part of the experiment, 7 sets of samples will be produces in order to compare the tensile strength of the pure polypropylene (PP), tensile strength for 0.5 wt%, 1 wt% and 2 wt% of pure MWCNTs in the MWCNTs-PP composite and then the tensile strength of 0.5 wt%, 1 wt% and 2 wt% of functionalized MWCNTs in MWCNTs-PP composite.

From all the samples, we can determine whether functionalized MWCNTs is better than pure MWCNTs and which weight percentage composition can give the best tensile strength. Weight percentage is chosen over volume percentage because it is easier to measure the weight of the PP pallets and MWCNTs powder instead of measuring their volume.

The tensile strength of the composites is measured using a 25K Universal Tensile Testing Machine with the test speed of 50.00 mm/min. From the graph below, the tensile strength for the polypropylene (PP) that was used in this experiment has the tensile strength of 28.42 MPa. Although from other papers, we can find PP can have tensile strength up till more than 40 Mpa, but it is not a concern for this project because we only want to compare how much increment in tensile strength that MWCNTs can give to the composite. Thus, as long as the same polypropylene is used constantly for all the samples, the result still can be justified.

The second graph represent the tensile strength of pure polypropylene, 0.5 wt%, 1 wt%, 2 wt% and 4 wt% of pure MWCNTs in the MWCNTs-PP composite. The MWCNTs-PP composite with 0.5 wt% of pure MWCNTs has the tensile strength of 29.4 MPa which has 3.46% increases as compares to the tensile strength of pure polypropylene sample.

As for the MWCNTs-PP composite with 1 wt% of pure MWCNTs, the sample has the tensile strength of 30.46 MPa. In comparison with the pure polypropylene sample and the 0.5 wt% sample, the 1 wt% sample has increase in tensile strength of 7.18% and 3.61% respectively. This shows that the composite with 1 wt% of pure MWCNTs is better than the pure polypropylene and the 0.5 wt% sample in terms of tensile strength.

On the other hand, the MWCNTs-PP composite with 2 wt% of pure MWCNTs has the tensile strength of 31.15 MPa. When compared with the previous three samples, the 2 wt% sample has higher tensile strength which is 9.61% higher than the pure polypropylene sample, 5.95% higher than the 0.5 wt% sample and 2.27% higher than the 1 wt% sample. This prove that sample with 2 wt% of pure MWCNTs has much higher tensile strength as compared to the previous three samples.

For the case of MWCNTs-PP composite sample with 4 wt% of pure MWCNTs, the sample as the tensile strength of 30.76 MPa. In comparison with the previous four samples, the 4 wt% sample has increase in tensile strength of 8.24% to pure polypropylene sample, 4.63% increase of tensile strength to the 0.5 wt% sample, 0.98% increase in tensile strength to the 1 wt% sample but a 1.25% decrease when compared to the 2 wt% sample.

There are two possibilities to why the 2 wt% sample has higher tensile strength to the 4 wt% sample. First is maybe because of the inefficient load transfer from the matrix to the composite because the there is too much reinforcement in the matrix. This causes some of the reinforcement to act as impurities instead of reinforcement. The second possibility is maybe because of the inefficient of the compression molding machine to disperse the MWCNTs in the composite matrix.

From this set of result, we can observe that the pure MWCNTs can help to increase the tensile strength of the composite sample and the composite with 2 wt% of MWCNTs has the highest increase of tensile strength as compared to the other composite samples.

The third graph represents the tensile strength of pure polypropylene sample, 0.5 wt%, 1 wt%, 2 wt% and 4 wt% of functionalized MWCNTs in the MWCNTs-PP composite;

When we observe this graph and compare it with the previous graph of data, it is obvious that there are much more increment in tensile strength. For the case of 0.5 wt% of functionalized MWCNTs in the MWCNTs-PP composite, it has the tensile strength of 30.35 MPa which is higher than the pure polypropylene sample and the 0.5 wt% of pure MWCNTs sample. It is 6.79% and 3.23% higher than the two samples respectively.

As for the sample with 1 wt% of functionalized MWCNTs in the composite, it has the tensile strength of 30.89 MPa which is 8.68 % higher than the tenile strength of pure polypropylene sample, 1.41% higher than the tensile strength of the

MWCNTs-PP composite sample with 1 wt% of pure MWCNTs and 1.78% higher than the composite sample with 0.5 wt% of functionalized MWCNTs.

Next, the sample with 2 wt% of functionalized MWCNTs in the MWNTs-PP composite has the tensile strength of 31.78 MPa which is 11.82% higher than the pure polypropylene sample, 2.02% higher than the MWCNTs-PP composite sample with 2 wt% of pure MWCNTs, 4.71% higher than the composite with 0.5 wt% of functionalized MWCNTs and 2.88% higher than the composite with 1 wt% of functionalized MWCNTs.

Lastly, the MWCNTs-PP composite sample with 4 wt% of functionalized MWCNTs has the tensile strength of 31.11 MPa. It is 9.47% higher than the tensile strength of pure polypropylene sample, 1.14% higher than the tensile strength of the MWCNTs- PP composite with 4 wt% of pure MWCNTs, 2.5% higher than the composite sample with 0.5 wt% of functionalized MWCNTs, 0.71% higher than the tensile strength of the composite with 1 wt% of functionalized MWCNTs and 2.11% lower than the tensile strength of the composite with 2 wt% of functionalized MWCNTs.

Same case with the composite samples pure MWCNTs, the sample with 2 wt% of functionalized MWCNTs as reinforcement has the highest tensile strength which makes it the ideal composition for MWCNTs-PP composite in terms of weight percentage. This is because with lesser than 2 wt% of MWCNTs as reinforcement, it might not be enough to withstand the force applied and when there is more than 2 wt% of MWCNTs as reinforcement, they will clump together because too much reinforcement presence in the same matrix and will act as impurities instead of reinforcement.

By comparing the two graphs of data, we can say that the functionalized MWCNTs can result in much higher tensile strength when it is used as reinforcement as compared to pure MWCNTs as reinforcement. This is because of the dispersion arrangement of functionalized MWCNTs is much better and dispersed as compared to the pure MWCNTs which have been proven in the earlier result section through the FESEM images.

The purity of functionalized MWCNTs also played a huge part in making it a better reinforcement as compared to pure MWCNTs. With lesser impurities in the tubes of functionalized MWCNTs, it has better physical properties as compared to the pure MWCNTs which have some impurities presence in the tubes. This has also been proven through the earlier result section using TEM images.

The table below is the comparison of the result of tensile strength from this experiment with the paper from M. Awang [27]. The chemical functionalization technique used is the same which uses same chemical mixture and also same functionalization time. The only difference is the method used to produce the composite sample to be used in the tensile testing. The paper uses the melt mixing technique to mix the MWCNTs and polypropylene and uses injection molding machine to produce the dogbone sample for tensile testing. In this experiment, both the equipment used in the paper is not available. Thus, compression molding is used as alternative to produce the dogbone sample.

From the table, we can see that the composite produced from the previous paper has much higher tensile strength as compared to the composite produced in this experiment. Although high quality MWCNTs is used in this project, the tensile testing result is still lower than the previous paper’s tensile testing result which used low quality MWCNTs. In terms of equipment used, the previous paper has the upper hand because both melt mixing machine and injection molding machine can the ability to mix the materials while they are melting inside it. That is why the previous paper can get higher tensile strength because the MWCNTs in the polypropylene matrix are properly dispersed with the help of both the equipment.

In the case of this experiment, in which compression molding is used, the MWCNTs cannot be dispersed as efficiently in the polypropylene matrix as efficient as melt mixing machine and injection molding machine. This can be the main reason why the composites produced in this experiment is not as good as the precious paper’s composite samples in terms of tensile strength.

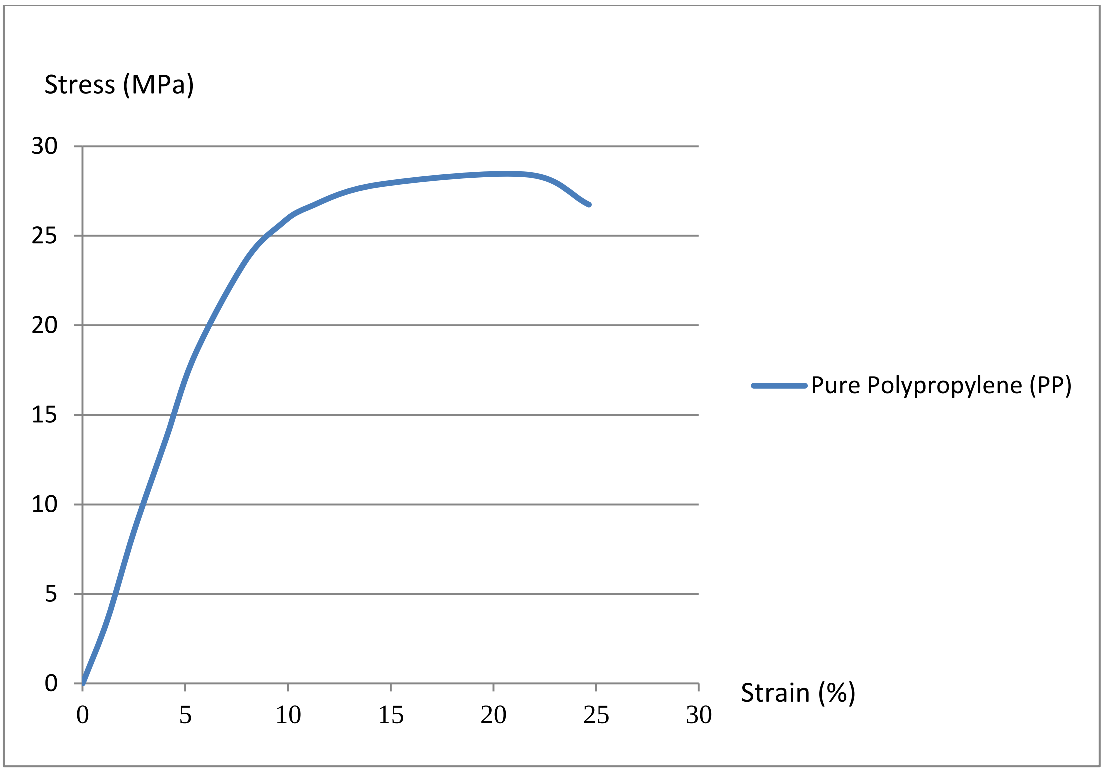

Figure 16. Stress-Strain Graph for Pure Polypropylene

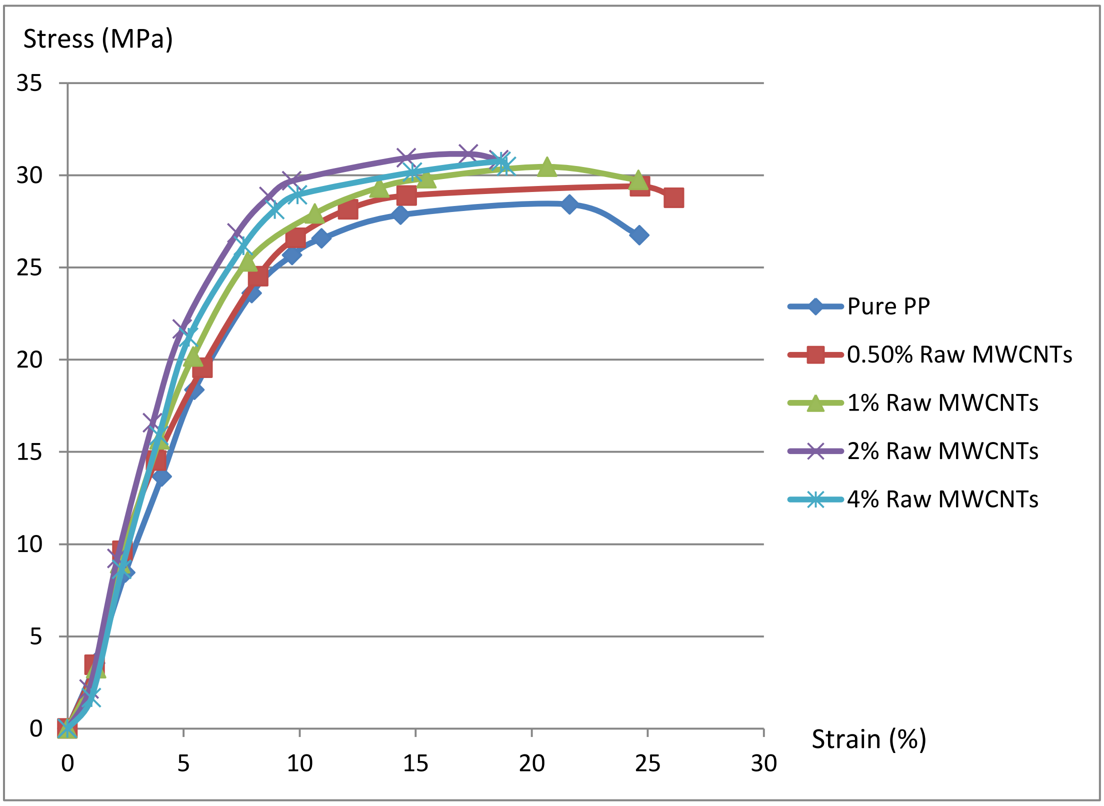

Figure 17. Stress-Strain Graph for Pure Polypropylene and Raw MWCNTs

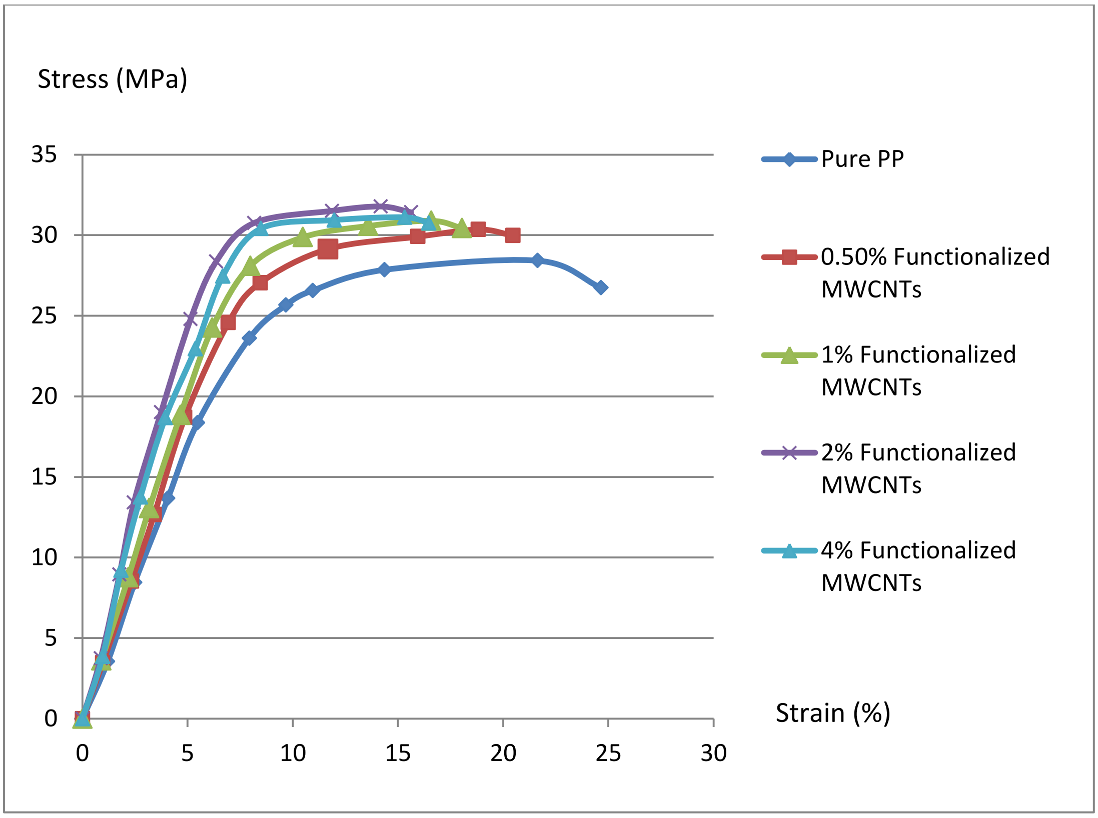

Figure 18. Stress-Strain Graph of Pure Polypropylene and Functionalized MWCNTs

Table 4. Tensile Test Result

Sample	Low Quality MWCNTs		High Quality MWCNTs	
	Tensile Strength (MPa)	Percentage Increase (%)	Tensile Strength (MPa)	Percentage Increase (%)
PP	28.96	-	28.42	-
PP + 0.5wt% Pure MWCNTs	30.31	4.64	29.40	3.46
PP + 1wt% Pure MWCNTs	32.47	12.11	30.46	7.18
PP + 2wt% Pure MWCNTs	33.32	15.04	31.15	9.61
PP + 4wt% Pure MWCNTs	32.56	12.42	30.76	8.24
PP + 0.5wt% Functionalized MWCNTs	30.83	6.45	30.35	6.79
PP + 1wt% Functionalized MWCNTs	32.90	13.59	30.89	8.68
PP + 2wt% Functionalized MWCNTs	33.63	16.09	31.78	11.82
PP + 4wt% Functionalized MWCNTs	33.98	17.32	31.11	9.47

CHAPTER 5

CONCLUSION AND RECOMMENDATION

According to all the results obtained, we can conclude that chemical functionalization is effective in both removing catalyst impurities inside the MWCNTs and also to alter their arrangement to be more dispersed. Some of the downside of this technique is that it can damage the tubes and shorten it. That is why the functionalization time of 2.75 hours is the ideal time period because it can remove the catalyst impurities and make the tube arrangements to be dispersed without damaging the tube too much.

In addition, the purification and dispersion of the MWCNTs helps in making a stronger MWCNTs-PP composite with higher tensile strength compared to the raw MWCNTs. It has also been proven that 2 wt% of MWCNTs that is functionalized chemically makes the ideal reinforcement in polypropylene matrix. Hence, both the objective of this experiment is successfully achieved.

For future recommendation, melt mixing machine and injection molding machines or twin-screw extruder should be used instead of compression molding machine to produce the composite sample. This is because the first machines have the ability to mix the MWCNTs into polypropylene which it is melting while compression molding cannot do so.

CHAPTER 6

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