CERTIFICATION OF APPROVAL

DEVELOPMENT AND MICROSTRUCTURAL ANALYSIS OF CARBON NANOTUBES REINFORCED COPPER MATRIX NANOCOMPOSITES USING PIM TECHNIQUE

By

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Approved by,

_____

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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 contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

The replacement of aluminum with copper in electronic industries had become breakthrough point. Due to copper's superior electrical conductivity, it enables conductor channel lengths and widths to be significantly reduced. The result is much faster operating speeds and greater circuit integration even up to 200 million transistors can be packed onto a single chip. Power requirements are now reduced to less than 1.8 volts. In recent years, thermal conductivity of electronic systems has been a significant issue. The reduction in material size becomes a challenge for electronic industry to produce high quality product with minimum cost. Nanostructure materials have attracted many researchers due to their outstanding mechanical and physical properties. While most researchers have focused on using CNTs to reinforce polymeric and ceramic matrices, CNT-reinforced metallic such as copper composites are quickly rising as attractive superior strength.

In this work, powder injection molding techniques were used to produce carbon nanotubes reinforced copper nanocomposite with unique mechanical properties. Pure copper (Cu) powder was mixed with multiwall carbon nanotubes (MWCNTs) to produce Cu-MWCNT composites. In the first phase of the work, Cu-25 vol. % MWCNT composite powders were mixed using internal mixer machine along with the binder system (70 vol. % of paraffin wax, 25 vol. % of high density polyethylene (HDPE) and 5 vol. % of stearic acid. Thermal gravity analysis (TGA) was used to evaluate the degradation temperature of the feedstock. The feedstocks then were processed into dumbbell shape using injection molding at 160^0C. The samples then undergo solvent and thermal debinding process at different temperatures and heating rates to obtain optimum parameter in producing defect free product. Next, the sample was sintered at different dwell time to obtain the best parameter. Finally characterization was done using FESEM to analyze Cu-CNT dispersion, powder morphology, CNT damage and phase analysis.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

In recent years, thermal conductivity of electronic systems has been a significant issue. The reduction in material size becomes a challenge for electronic industry to produce high quality product with minimum cost. These problems were overcome by replacing aluminum usage with copper and integrating carbon nanotubes to improve the thermal conductivity of electronic device. However, the production of copper reinforced carbon nanotubes using traditional technique such as forging, casting, and extrusion and machining has its limitations in shape details, precision, time consuming, need of secondary machining and its highly cost. As an alternative, powder injection molding technique is used to study on the development and characterization of Multiwalled Carbon Nanotubes (MWCNTs) reinforced Copper (Cu) nanocomposites.

1.2 Problem Statement

In the process to clarify the purpose of the research was being carried out, the problem statement are divided into two sections:

1.2.1 Problem Identification

The challenge in thermal management in electronic industries needs an effective technique to save cost and to produce free defect composites. It is true that there are quite a number of existed traditional methods, but the effectiveness of those methods was not satisfied economically. Therefore, there is a need of finding a new method to

enhance the existed method, which is more effective and reliable. Through the researchers being done, Powder Injection Molding (PIM) is a promising method to overcome the problems.

It has been theoretically studied that the reinforcement of Multiwalled Carbon Nanotubes (MWCNTs) in Copper nanocomposites can be simply improved by its thermal and electrical dissipation.. With respect to that, the PIM technique is used on proving those theoretical studies and finding the best parameter of production.

1.2.2 Significant of Project

The aim of this research is to understand and experiment the various parameter involve in PIM debinding and sintering stage. In order to meet the time frame of the project, two parameters is evaluated which are temperature, time and heating rate. Beside Field Emission Scanning Electron Microscopy (FESEM) is used to analyze the microstructure of the nanocomposites.

1.3 Project Objectives

The main objective of this research is to obtain the optimum parameter at debinding and sintering stage.

There are also a few other objectives which are:

- To develop that would produce free defect.
- To analyze the microstructure/characteristic using Rheometer, FESEM and TGA.

1.4 Scope of Study

For the scope of study, Multiwalled Carbon Nanotubes (MWCNTs) reinforced copper are develop and characterize using powder injection molding technique. Feedstocks are produce at a composition of MWCNTs from 25% using mixer. Feedstocks viscosities are then evaluated using rheometer at different load and temperature. The experiment also includes debinding process at two stage which are

solvent debinding and thermal debinding. Sintering process is the final stage of experiment and analysis of MWCNTs/Cu microstructure is done using FESEM. Three different parameters have been chosen to conduct the study. At different stage different parameter will be fixed throughout the experiment to compare the results of each study that will be carried out. The scope of the study will be on the three different solvent debinding temperatures, three different heating rates during thermal debinding, and three different dwell times during sintering.

1.4.1 The relevancy of the Project

This project will focus on the powder injection molding technique at different temperature, heating rate and dwell time and the microstructure analysis of Cu/MWCNTs. This topic is related to the course of Introduction to Material Science & Engineering, Manufacturing Technology I & II, Engineering Materials and Advance Engineering Polymer, Ceramics & Composites to perform research for this project.

1.4.2 Feasibility of the Project

The project is divided into four sections. Section one will basically be on finding, collecting, and reading of journals, technical papers, and books of the research topic. The second section of the project will be mainly on mixing of MWCNTs and Cu and Injection Molding. The third section of the project is the debinding and sintering phase. The last section will then be done to analyze the microstructure of MWCNTs/Cu to choose the optimum parameter.

CHAPTER 2

LITERATURE REVIEW

2.1 Copper (Cu)

Copper is the preferred and predominant choice in the electrical industry because of its high conductivity, both electrical and thermal. Copper they have one s-orbital electron on top of a filled d-electron shell and are characterized by high ductility and electrical conductivity. The filled d-shells in these elements do not contribute much to the inter-atomic interactions, which are dominated by the s-electrons through metallic bonds. Contrary to metals with incomplete d-shells, metallic bonds in copper are lacking a covalent character and are relatively weak. This explains the low hardness and high ductility of single crystals of copper [1].

2.2 Carbon Nanotubes (CNTs)

Since the discovery of carbon nanotubes (CNTs) in 1991 by Iijima [2]**,** Carbon nanotubes (CNTs) are increasingly attracting scientific and technological concern as an ideal reinforced material to improve the mechanical performance of many materials. The exceptional small diameters as well as the high Young's modulus, tensile strength, and unique conductivity, CNTs are an attractive reinforcement material for lightweight and high-strength metallic matrix composites [1]. There is a new interest in exploiting these properties by incorporating Carbon Nanotubes into some form of matrix. Several researches have shown that Carbon Nanotubes can considerably enhance the mechanical and ceramic matrix during last decade. In carbon nanotube/polymer nanocomposites, the addition of carbon nanotubes as reinforcement improves the strength of the polymer matrix by several times. Composites materials containing conventional carbon fibers in metal matrix, such as aluminum or magnesium, are used in a number of specialist applications. Such composites combine low density with high strength and modulus, making them attractive to aerospace industry. However it is important to have homogeneous

dispersion of carbon nanotube in metal matrix to avoid agglomeration of carbon nanotube.

2.3 Carbon Nanotubes and Copper Nanocomposites

As it was mentioned earlier, CNTs have extremely high mechanical and electrical properties in addition to their ultra low density, which makes them very attractive and appropriate for use as reinforcement in composite materials. Using CNT in PIM manufacturing is very promising because this could be the way for producing lightweight, ultra high strength, and stiff products made out of Metal Matrix-Nanotubes. Morelli [3] emphasizes that there are two major problems that face scientists and researchers in manufacturing CNT reinforced composites which are: achieving a homogeneous and uniform dispersion of CNT in the matrix, and forming a strong bond at the CNT-metal interface. Lots of papers dealing with these problems have been published and some researchers were able to come up with techniques that deal with the dispersion problem, but there is no study up till now that shows a method for enhancing the bond between CNT and their matrix.

2.4 Powder Injection Molding

Powder injection molding is a cost effective method in producing simple or complex part close to final dimension at production rate which range from few hundred to several thousand parts per hour. These characteristics have lead to an evolving and steadily growing market potential. An increasing demand on numbers and geometric complexities of metallic products caused increasing problems in the manufacturing of the products [4]. A lot of techniques developed to overcome the problems of geometric complexities, where most of them are orienting themselves to the so called “near-net-shape” techniques such as die pressing and sintering of metal powder. One of the new techniques developed is known as powder injection molding (PIM). The study on PIM concern on three main processes: injection molding of a binder/powder mixture, thermal or catalytic debinding and sintering [5-6]. Figure 2.1 shows a schematic view of the synthesis process based on the PIM method.

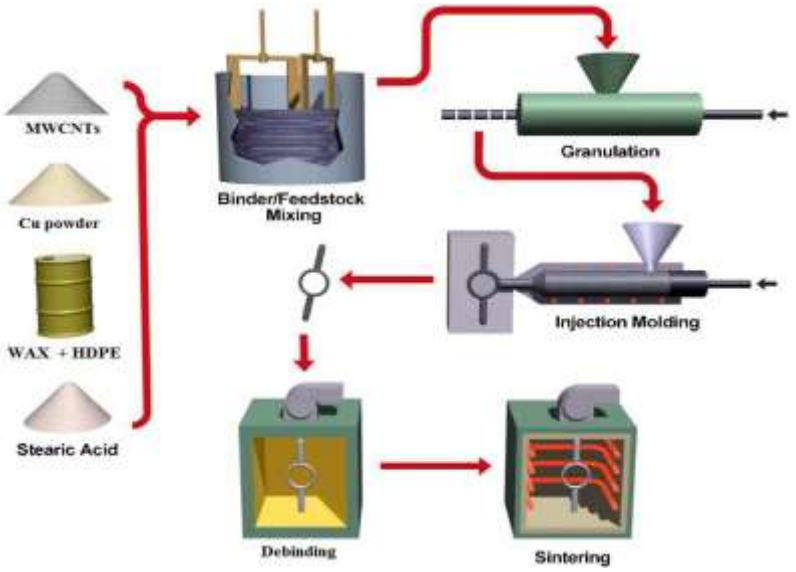

Figure 2.1: Powder Injection Molding process [7]

Usually, manufacturing techniques for porous material comprise compacting a metal powder in a die and subsequently machining and etching to achieve the final geometry. Die compaction is restricted not only in its shape-making capabilities due to tooling and compaction constraints, but also in its ability for producing an isotropic pore size, permeability, and density. The product of this technique has high densities in the top and bottom of the sample but less density in the middle of the compact. This problem increases as the height to width ratio increases, making long, thin parts not viable to manufacture uniformly [8]. In addition a selective laser sintering technique also can produce net-shape components, but it has limited dimensional precision and its production rate is in the order of hours rather than seconds. Therefore, a perfect opportunity exists for the mass manufacturing of net-shape porous structures with comparatively isotropic pore structure by the use of powder injection molding [8].

2.4.1 Mixing

The feedstock for molding is prepared through mixing a suitable ratio of powder and binder. It is important that the mixture is homogeneous, free from agglomeration and contains no porosity [9]. Any deficiencies in mixing cannot be altered in subsequent processing steps. Mixing deficiencies only can be seen at subsequent processing steps such as molding, debinding and sintering [9].

The use of too-little binder may create voids in the mixture and results in a high viscosity feedstock that is difficult or impossible to mold [9] in contrast, excessive binder gives a low molded strength and may cause binder–powder separation during molding: this causes an inhomogeneous part which may contribute to dimensional problems [10]. Excessive binder will slow the debinding process and may cause part slump when the particles settle or migrate during debinding [11]. The dimensional changes during sintering will also be larger. In order to establish a suitable powder loading, the following binder system as in table 2.1 composition is evaluated to attain high solid loading and homogeneity.

Table 2.1: Binder formulations developed for viscosity measurement. [12]

Binder ingredient	**B1**	**B2**	**B3**
Parafine wax	55	65	70
HDPE	40	30	25
Stearic Acid	5	5	5

Binder B3 was selected due to its lower viscosity and with an objective to achieve higher solid loadings [12].

Other mixing parameters that could influence the homogeneity of the feedstock [9, 13] are the type of mixer and mixer blades, the mixing speed and the temperature, the mixing time and the sequence. The binder and powder characteristics will also affect homogeneity.

The mixer blades are lighter in construction and have a relative smaller surface area as opposed to a horizontally mounted blade [9]. Even though higher mixing speed is efficient in breaking agglomerates, it could induce micro-bubble formation in the feedstock, creating inhomogeneity [9, 14]. A lower speed helps to prevent air trap but is not effective in breaking the agglomerates. A balance needs to be achieved and a medium speed may be the most suitable. Too long a mixing time can cause

degradation of binder components [9]. The mixing temperature has also an effect on dispersion since of its effect on feedstock rheology [9]. It was reported [15] that using a temperature very close to the melting of the polymer caused extensive particle–particle interactions and poor dispersion, these being attributed to poor wettability of the polymer at this temperature.

Formulations of copper powder and multiwalled carbon nanotubes with binder, B3 were prepared using a Z-blade mixer as shown in Figure 2.2.

Figure 2.2: Z- Blade Mixer [12]

Mixture of copper/binder was prepared at a temperature of 160°C and Z-blade rotation speed of 50 rpm for 40 minutes [12]. For preparation of copper/ MWCTNs feedstock , copper and MWCNTs were dry blended in a ball mill for 20-30 minutes followed by compounding in a Z-blade mixer at 140°C [12, 16]. In order to obtain uniform dispersion of MWCNTs and copper powder in binder, mixtures were solidified and granulated to > 5 mm for powder injection molding [12].

2.4.2 Injection Molding

After mixing process, the feedstock was injected at 160°C and 4 bars with the mold temperature 30-40 °C and samples with dumbbell and strip were obtained [18]. The injection molding was performed in a short time to match the injected amount with the mold size. No sign of defects within the samples observed after the injection molding process. Figure 3 shows the FESEM micrograph of Cu/MWCNTs feedstock [17].

Molded parts may come out to be intact and free of visible defects, but the density gradient in them may cause dimensional variation of distortion during sintering. Flow-induced orientation during molding could be a possible source of defects during debinding [9, 18] and [9,19]. By varying the molding parameters, molding defects can be overcome.

Some of the defects due to inappropriate selection of molding parameters cause crumbled edges and cracks, are shown in figure 2.3 below. Crumbled edges were seen at the low injection speed. The defects are reduced at higher injection speed profile. However, too high an injection speed caused an increase in the peeling of the part surface. Using the best speed, the packing pressure was varied. High packing pressure reduced crumbling but subjected the part to severe stresses, causing cracks. Too low a pressure does not allow sufficient material to be packed into the cavity to compensate for shrinkage during solidification, which may result in voids, porosity or internal cracks due to shrinkage.

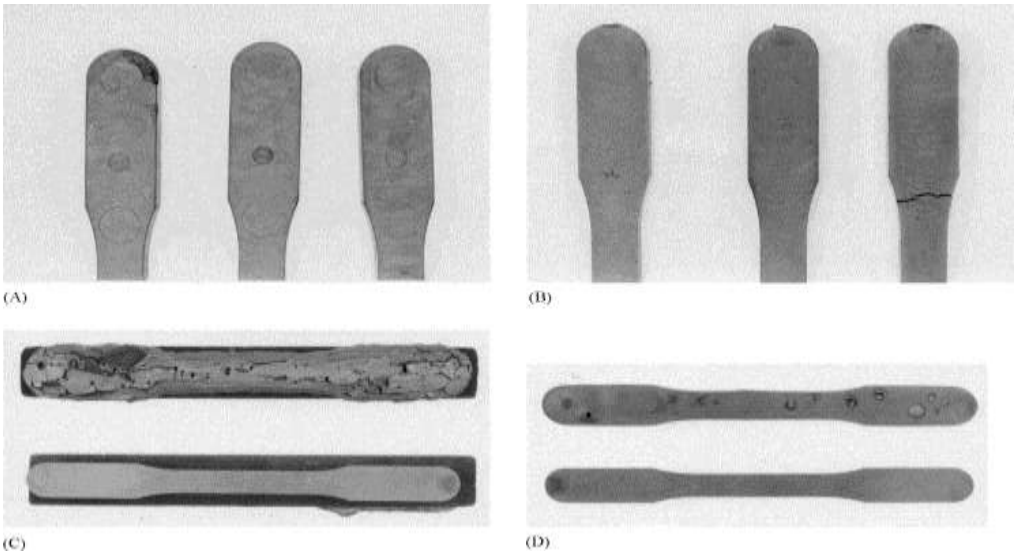

Figure 2.3: Defects in PIM (A) Crumbled edges — speed profile (left to right (B) Cracks — packing pressure profile (left to right (C) Flaking of a debound part (upper picture) for the debinding & molded part (lower picture). (D) Blisters on a debound part (upper picture) & Molded part (lower picture) [9]

2.4.3 Debinding

Debinding process consist of two stages which are solvent and thermal debinding. The debinding schedule comprises three main elements: heating rate, debinding temperature and debinding time. A suitable combination of the three parameters will produce a defect-free part which is one of the main objectives of this study.

To reduce the possibility of defects with safe and fast binder removal, the multi-component binder chosen includes the lower stability components of paraffin wax and stearic acid, which are removed in early stage of debinding, and generate pore channels [8, 17]. It is considered that after removing some percent of the binder, there exists some interconnected capillary porosity inside of the samples which makes leaving of gaseous products in subsequent thermal debinding easy in short time. Since nearly most of binder was removed in solvent debinding step, subsequent thermal debinding can be performed with higher speed in comparison with usual thermal debinding process [19].

2.4.4 Sintering

Sintering gives strong antiparticle bonds and removes or reduces the void space by densification. Hence, sintering lead to substantial shrinkage in the PIM parts [9]. Several parameters influence the sintering process: these include initial density, material, particle size, sintering atmosphere and temperature, sintering time and heating rate [9, 21, 22]. A rapid heating rate can trap surface contaminant within the part and cause degradation properties. On the other hand, too slow a heating rate will give poor densification and inferior properties. Too high a temperature or too long a sintering time will cause distortion, slumping, excessive grain growth and even bloating [9].

2.5 Copper and Multiwalled Carbon Nanotubes Characterization

Many techniques are used for characterization of multiwalled carbon nanotubes reinforced copper nanocomposites properties. To understand structure-property relationships, some characterization techniques are employed. The characterization methods used in this study is to analyze of the morphology and the physical properties, of the nanocomposites. The properties of multiwalled carbon nanotubes

reinforced copper strongly depend on their composition and interfacial interaction. The interfacial interaction between copper and multiwalled carbon nanotubes strongly affects mechanical and thermal other properties of the nanocomposites. Therefore different types of characterization have been used to clarify the nanocomposites. The types of Characterization used copper and multiwalled carbon nanotubes are Rheometer (Rheometer), Field Emission Scanning Electron Microscopy (FESEM), Thermal gravity analysis (TGA).

CHAPTER 3

METHODOLOGY

3.1 Introduction, Key Milestones & Gantt Chart

The methodology is formulated based on powder injection molding production and testing. Summary of methodology is shown in figure 3.1 below.

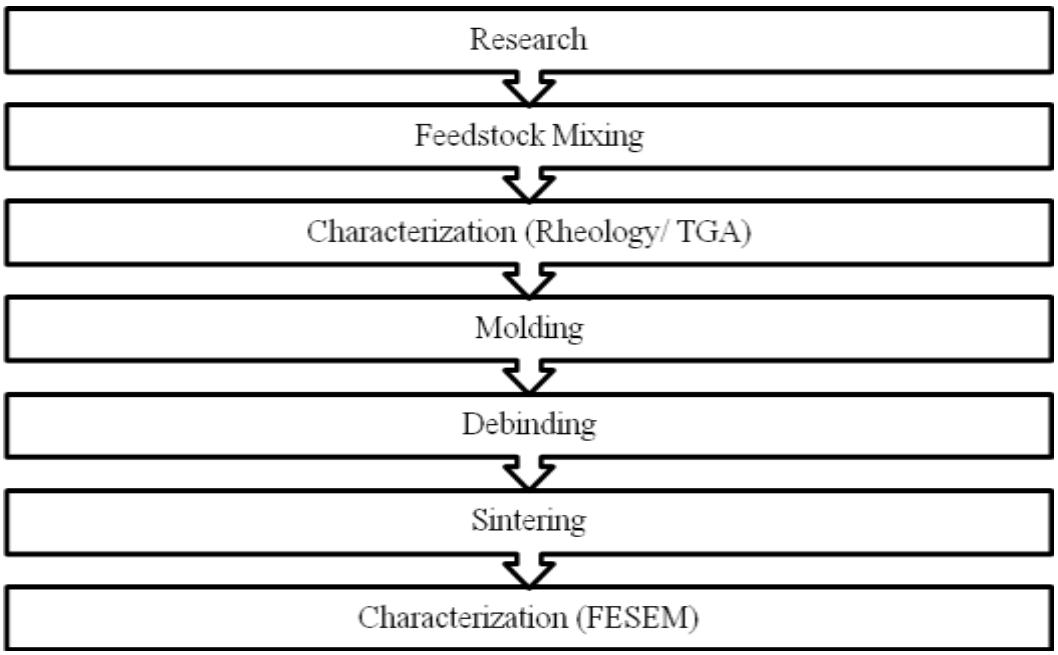

Figure 3.1: Flow chart of project methodology

The key milestone and datelines for each activity are specified in the Project Gantt Chart in Appendix A and Appendix B.

3.2 Research Methodology

Different findings and methodologies are gathered from the research work of other researchers and to be incorporated in this project. First and foremost, various journals and technical papers were read through the get the general understanding on the project. It is also needed to identify the objective of this project and to come up with a proven method to run the experiment. The complete flow of the project is shown in the flow chart below.

3.3 Project Activities (Experimental Works)

Experimental works consist of the stages in Powder injection molding process which is mixing, molding, debinding and sintering. The focus for this study will be on debinding and sintering stages.

3.3.1 Mixing

In the mixing stage the following materials will be used:

a) The copper powder (99.95% purity) of spherical in shape was used in this study. As in [17] the copper powder produced by gas atomization and supplied by Sandvik Osprey LTD, UK. Particle size distribution of copper powder was >22 μm.

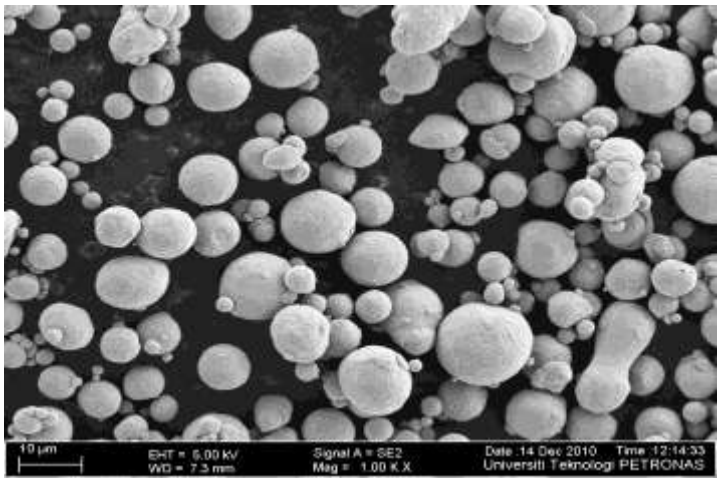

Figure 3.2: SEM image of copper powder shows spherical shape [17]

b) The multi-walled carbon nano tubes (MWCNTs) used for this research was supplied by Shenzhen Nano-Technologies Port Co., Ltd., China [17]. The dimensions of MWCNTs were: diameter 10-20nm, length 5-15 μm. The purity is 95-98% and ash content of ≤0.2 wt %.

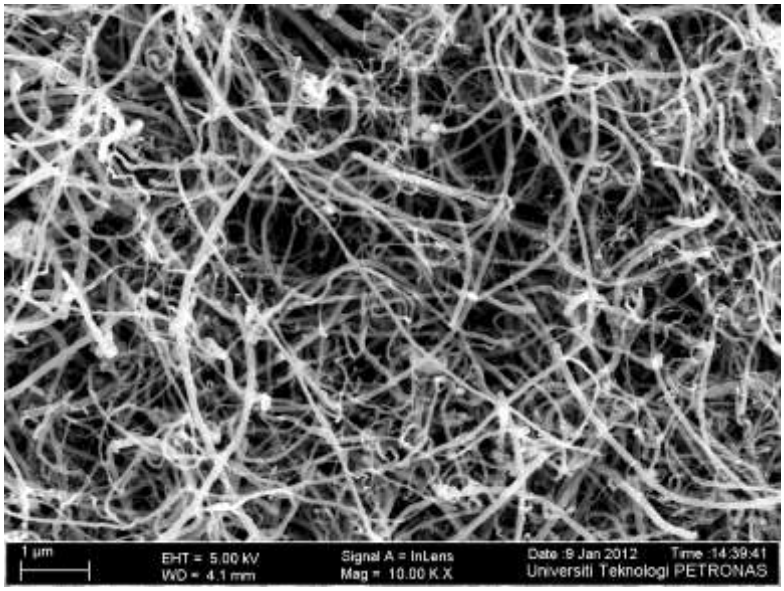

Figure 3.3: FESEM image of MWCNTs

The Properties of the copper and MWCNTs are shown in table 3.1 below.

Table 3.1: Properties of the copper and MWCNTs

Properties	**Materials**	
	Copper	**MWCNTs**
Thermal Conductivity	401 W/m.K	1200~ 3000 W/m.K
CTE	17.0x 10^{-6} /ºC (20-100°C)	Theoretical negligible
Density	8.96 g/cm^3	1.33~1.4 g/cm^3

c) The binder system consists of three ingredients. Paraffin wax (PW) is a major binder component supplied by Merck. High density polyethylene (HDPE) was supplied by Titan Pet chem. (M) Sdn Bhd, Johor, Malaysia as a minor binder component and stearic acid (SA) was supplied by ACROS organics as a surface active agent or flow promoter [17]. The properties of the binder system are shown in table 3.2 below.

Table 3.2: Properties of the binder system [17]

Binder ingredient	**Density (g/cm3)**	**Melting Temperature (°C)**
Parafine wax	0.90	60-65
HDPE	0.95	130
Stearic Acid	0.96	67-69

The mixing process was carried out using Z-blade mixer at temperature of 160°C and rotation speed of 50 rpm for 40 minutes. Ensuring uniform dispersion of MWCNTs and copper powder in binder, mixtures were solidified and granulated to > 5 mm for powder injection molding [17]. Table 3.3 below shows the composition to prepare 25% Cu/MWCNTs nanocomposites and figure 3.4 below shows the FESEM image of the 25 % Cu/MWCNTs feedstock.

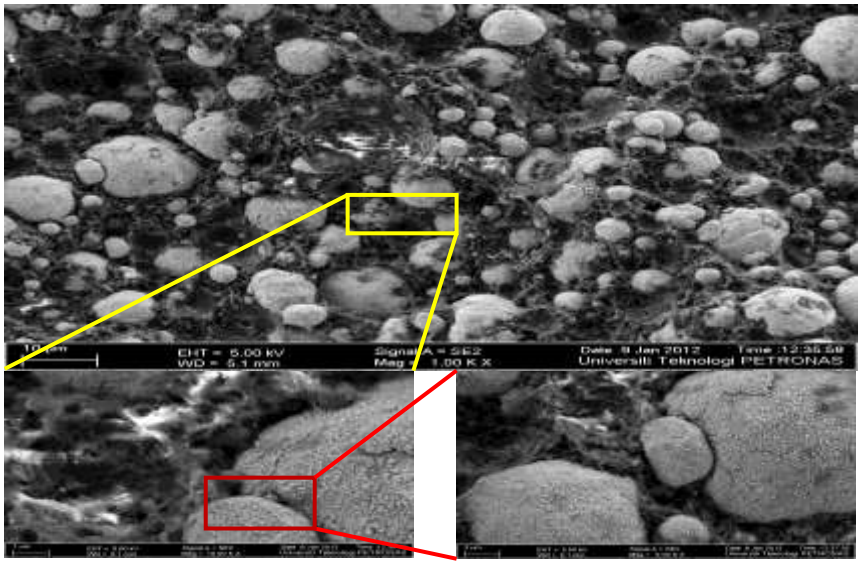

Figure 3.4: FESEM image of Feedstock 25% Cu/MWCNTs

Table 3.3: Composition of the samples

<table>
<tr><th colspan="2">Sample</th><th colspan="3">Volume %</th></tr>
<tr><td colspan="2">Copper  </td><td colspan="3">34</td></tr>
<tr><td colspan="2">MWCNTs  </td><td colspan="3">25</td></tr>
<tr><td rowspan="3">Binder System</td><td colspan="3">41</td></tr>
<tr><td>PA</td><td>HDPE</td><td>SA</td></tr>
<tr><td>70</td><td>25</td><td>5</td></tr>
<tr><td>  </td><td>  </td><td>  </td></tr>
</table>

3.3.2 Molding

The feedstock was injected at 170°C and 4 bars with the mold temperature 30-40 °C and samples with dumbbell and strip were obtained. The injection molding was performed in a short time to match the injected amount with the mold size. No sign of defects within the samples observed after the injection molding process. Figure 3.5 below show the molded sample of 25% multiwalled carbon nanotubes reinforced copper.

Figure 3.5: Molded sample 25 % Cu/MWCNTs

3.3.3 Debinding

Solvent Debinding

At this stage, the temperature and time are varied to obtain the optimum debinding parameter. Three temperatures were evaluated which are $6^0$0C, 65^0C and 70^0C for a duration of 7 hours. The samples were immersed in heptanes and put into the circulating water bath machine. The weight of each sample is measured before and after being immersed. Since most of the binder removed at this stage, there exists some interconnected capillary porosity inside of the samples which makes leaving of gaseous products in subsequent thermal debinding in short time.

Thermal Debinding

Thermal debinding process was evaluated at three different heating rate which are 1^0C/min, 3^0C/min and 5^0C/min. All the other parameter for the thermal debinding was fixed such as the temperature and dwell time. The temperature is set to be 500^0C and dwell time is 1.5 hours (90 minutes).

3.3.4 Sintering

During sintering, temperature increased from 500 °C to the sintering temperature with the rate of 8°C/min under argon atmosphere and held at that temperature for different hours which are 1 hour, 1.5 hours and 2 hours. Sintering was performed at 1050^0C. For the optimum dwell time the dwell time is varied.

3.3.5 Characterization

a) Rheology

Rheology test is conducted using a capillary Rheometer (Shimodzu flow tester CFT-500D), Figure 3.6, using a capillary die of 1-mm diameter and length of 10-mm was used to measure the viscosity of binder systems to identify a suitable binder with minimum viscosity to achieve higher loading of solids [12]. Binder granules were

filled into rheometer barrel heated to 160 °C and slight pressure was applied using rheometer ram and allowed for 5-10 minutes to reach equilibrium temperature throughout the materials [12]. The materials were extruded through the capillary die and time taken was recorded. Volumetric flow of melt was calculated for shear rate and corresponding shear stress was calculated to determine the viscosity of the binder. The viscosity of binder was measured over a shear rate of approximately 2000 1/s [12].

Figure 3.6: Capillary rheometer

b) Thermal Gravity Analysis (TGA)

The thermal degradation properties were evaluated using Perkin Elmer, thermal gravimetrical analyzer, under nitrogen atmosphere and heating rate. The TGA curves can be used for determine the upper limit of the melt temperature during injection molding and temperature during thermal debinding process.

c) Field Emission Scanning Electron Microscopy (FESEM)

FESEM used to evaluate the morphology and the MWCNTs dispersion throughout copper. Besides, the FESEM is evaluated after each stage such as after debinding and sintering at different magnification from 5k to 50 k.

3.4 Tools Required

I. Binder/Feedstock mixer

II. Capillary Rheometer

III. Injection molding machine

IV. Circulating water bath machine

V. Tube Furnace

VI. Thermal gravimetrical analyzer (TGA)

VII. Scanning electron microscopy (SEM)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Feedstock Characterization

Thermal Gravity Analysis

Figure 4.1 below shows the TGA curve of the feedstock, and indicates that the degradation starts at 170°C and ends at 500°C. Therefore to avoid the degradation during mixing or injection molding processes the processing temperature must be lower than that temperature (170°C) and temperature of 500^0C for thermal debinding. Hence we choose 160° for mixing and molding process to avoid the degradation of feedstock.

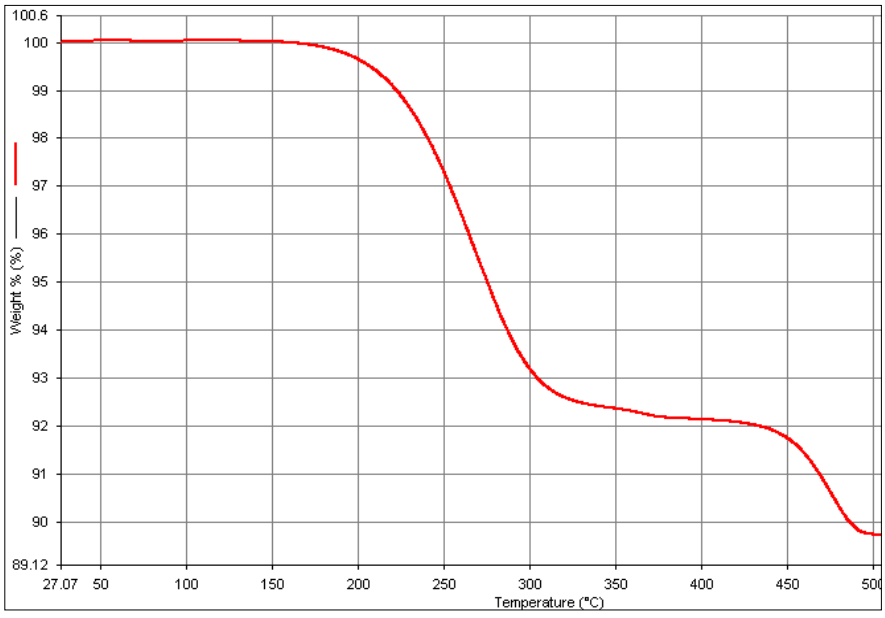

Figure 4.1: TGA result for 25% Cu/MWCNTs feedstock

4.2 Solvent Debinding Results & Discussion

Experimental result of Solvent Debinding

Table 4.1: Solvent Debinding result at temperature 60 ^{0}C

Sample	Wt before (g)	Wt after (g)	Binder Weight (g)	ΔWt(g)	Removal Wt %
1	3.036	2.853	0.326	0.183	56.21
2	2.644	2.478	0.284	0.166	58.55
3	2.072	1.936	0.222	0.136	61.21
4	2.749	2.563	0.295	0.186	63.10
5	4.446	4.117	0.477	0.329	69.01
6	4.206	3.894	0.451	0.312	69.18
7	2.391	2.213	0.256	0.178	69.42

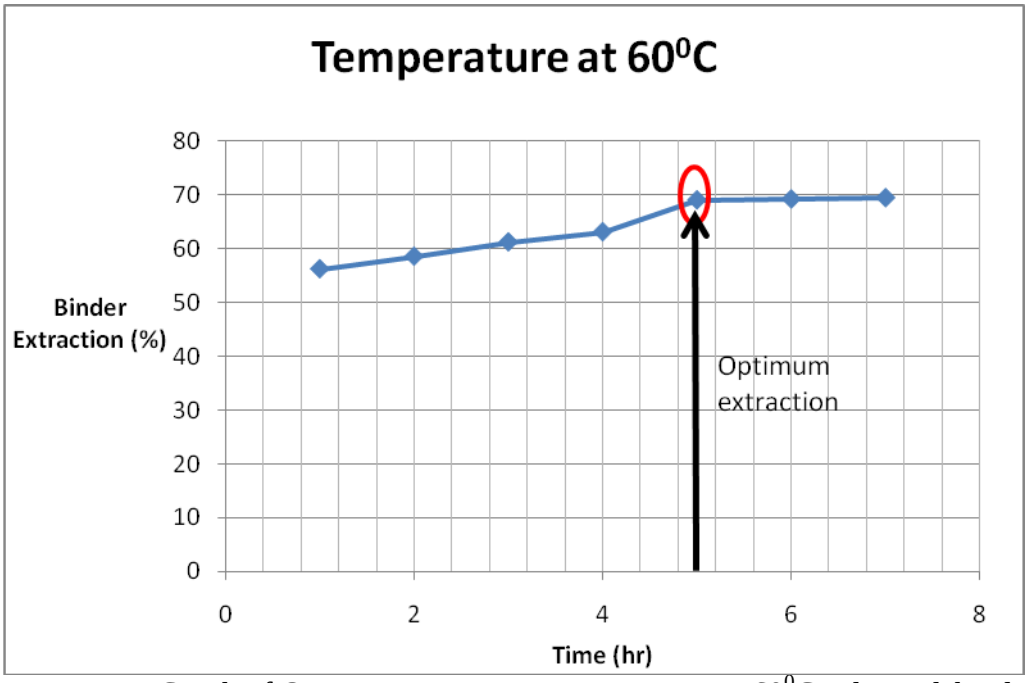

Figure 4.2: Graph of Optimum extractions at temperature 60^{0}C solvent debinding

Table 4.2: Solvent Debinding result at temperature 65 ^{0}C

Sample	Wt before (g)	Wt after (g)	Binder Weight (g)	ΔWt(g)	Removal Wt %
1	2.360	2.256	0.169	0.104	61.53
2	2.894	2.764	0.207	0.130	62.72
3	2.972	2.819	0.213	0.153	71.88
4	2.439	2.313	0.175	0.126	72.13
5	2.784	2.640	0.199	0.144	72.22
6	2.215	2.100	0.159	0.115	72.49
7	3.015	2.858	0.216	0.157	72.71

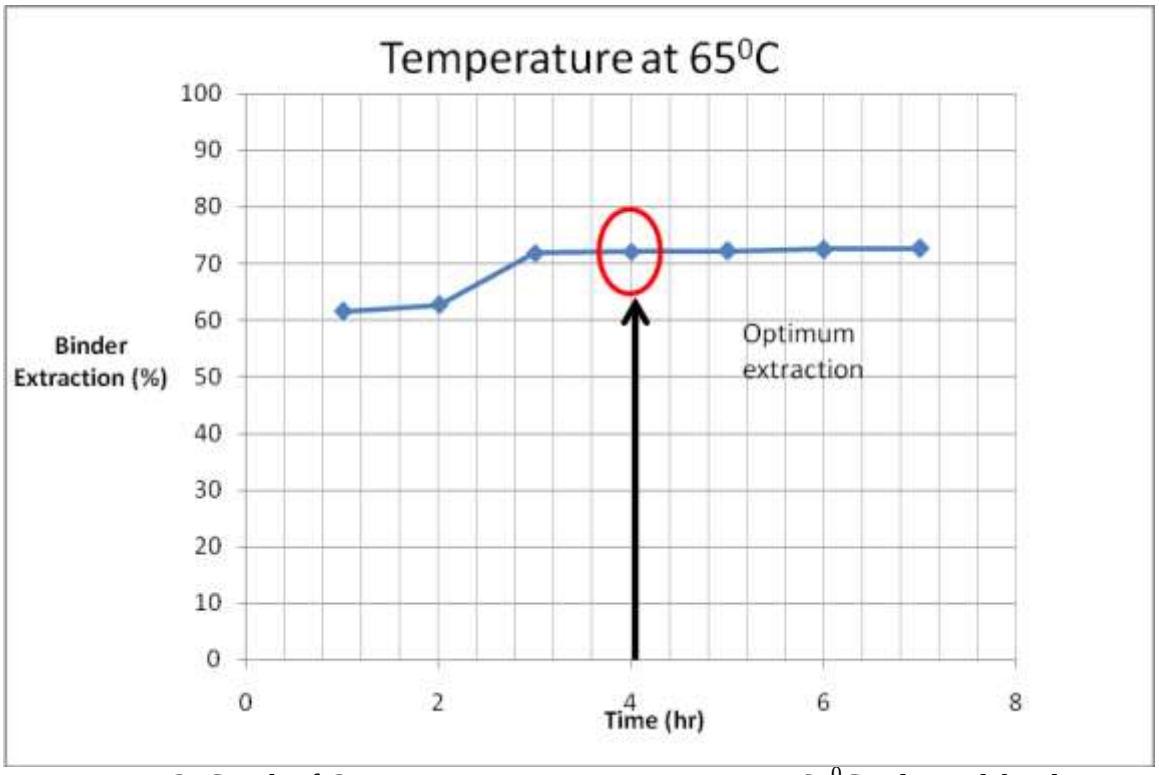

Figure 4.3: Graph of Optimum extractions at temperature 65^{0}C solvent debinding

Table 4.3: Solvent Debinding result at temperature 70 ^{0}C

Sample	Wt before (g)	Wt after (g)	Binder Weight (g)	ΔWt(g)	Removal Wt %
1	2.766	2.647	0.207	0.119	57.58
2	2.964	2.825	0.221	0.139	62.76
3	2.484	2.345	0.186	0.139	74.89
4	2.873	2.711	0.215	0.162	75.52
5	2.885	2.722	0.216	0.163	75.52
6	2.518	2.376	0.188	0.142	75.52
7	2.370	2.236	0.177	0.134	75.52

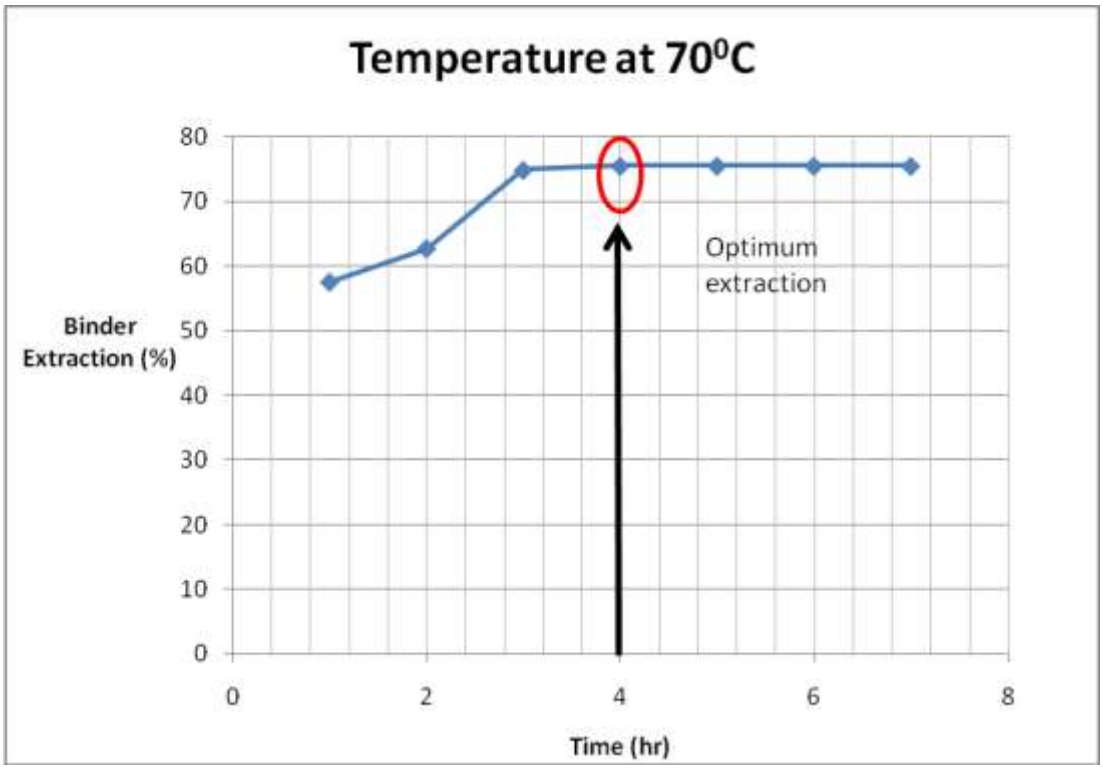

Figure 4.4: Graph of Optimum extractions at temperature 70^{0}C solvent debinding

Characterization result of Solvent Debinding

Figure 4.5 and 4.6 below show the results of solvent debinding for 25% Cu/MWCNTs at time 1 hour and temperature 70^0C.

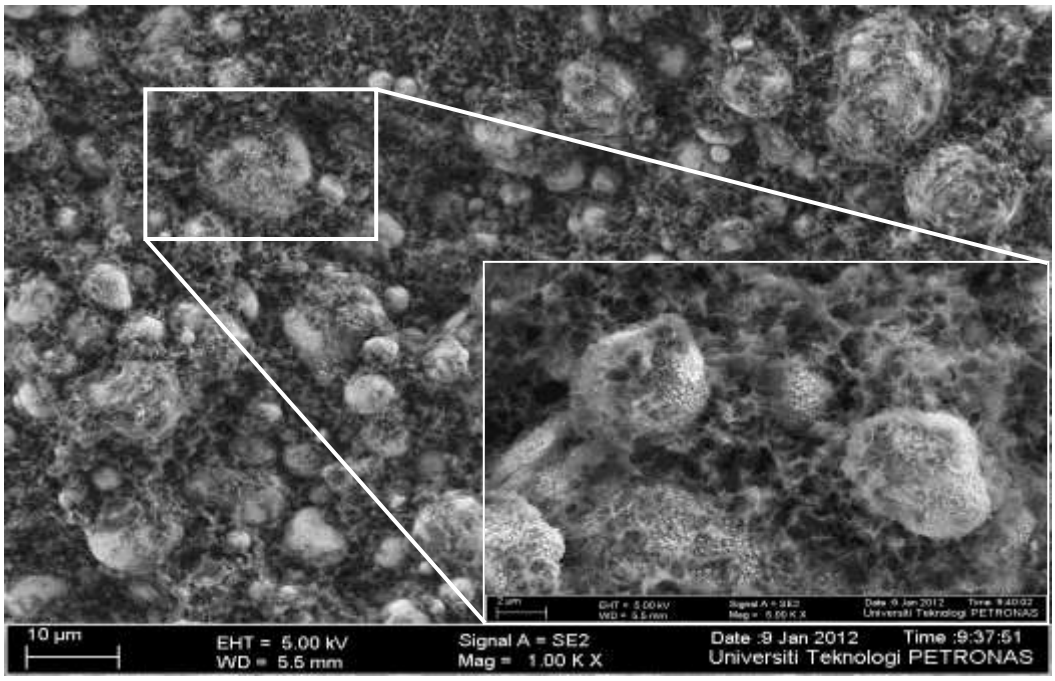

Figure 4.5: FESEM result for Solvent Debinding at 70^0C time 1 hour with 1 KX and 5 KX Mag.

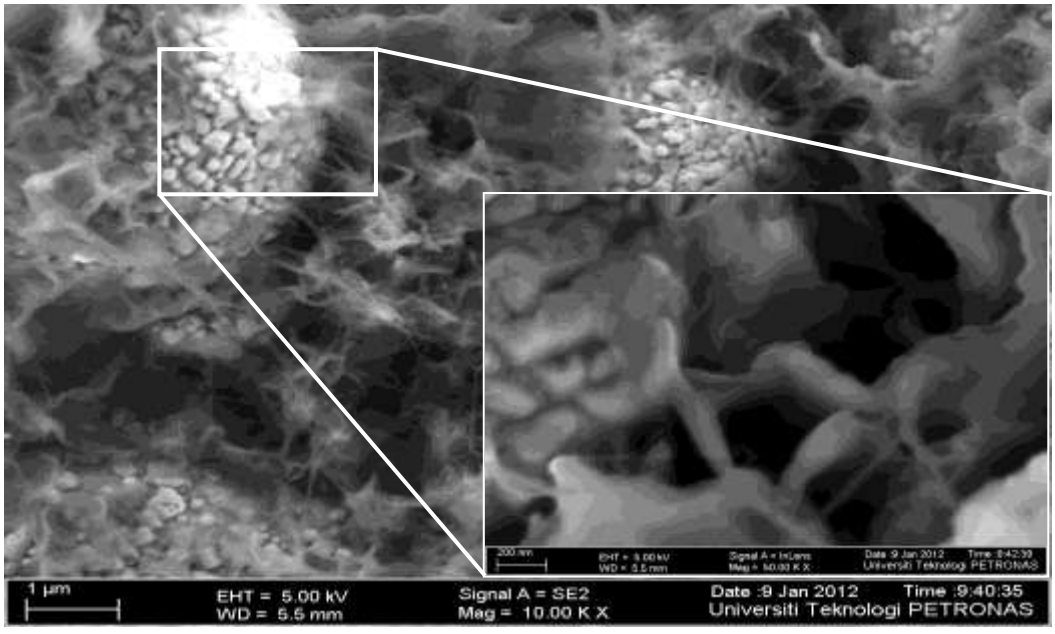

Figure 4.6: FESEM result for Solvent Debinding at 70^0C time 1 hour with 10 KX and 50 KX Mag.

Figure 4.7 and 4.8 below show the results of solvent debinding for 25% Cu/MWCNTs at time 3 hour and temperature 70^0C.

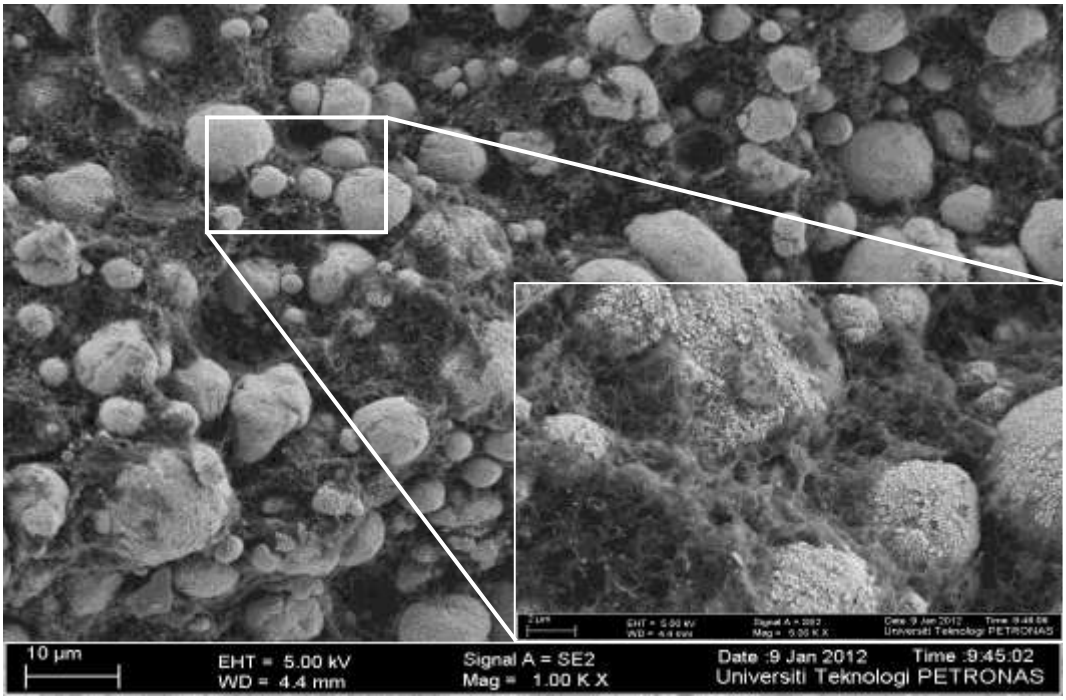

Figure 4.7: FESEM result for Solvent Debinding at 70^0C time 3 hour with 1 KX and 5 KX Mag.

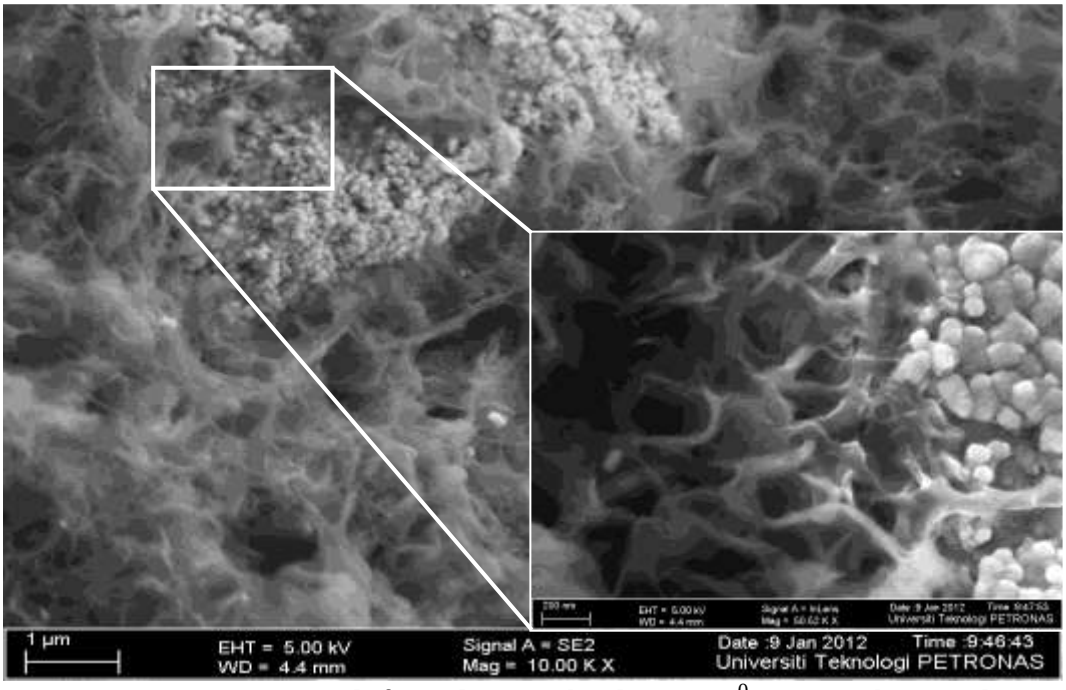

Figure 4.8: FESEM result for Solvent Debinding at 70^0C time 3 hour with 10 KX and 50 KX Mag.

Discussion

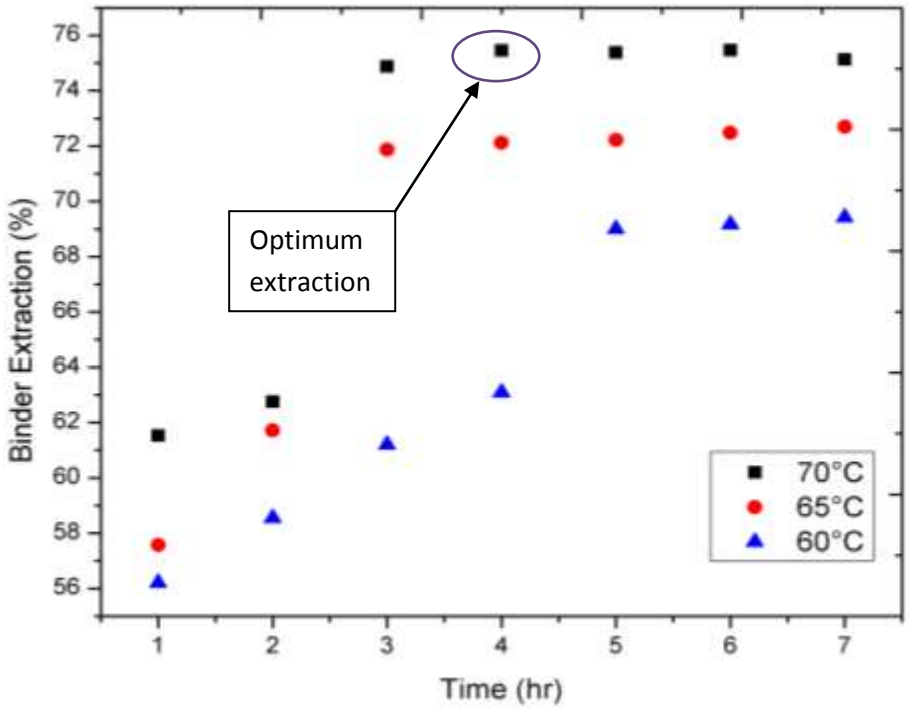

Figure 4.9: Comparison of Solvent Debinding Results at Different Temperature.

From the result shown in figure 4.9 above, we can observe that at temperature 70^0C the highest extraction of the binder system consist of of paraffin wax and stearic acid is been extracted. The result also indicates 4^{th} hours as the optimum time for extraction. At the 4^{th} hour and temperature of 70^0C we can conclude the optimum extraction occurs. The removal of paraffin wax and stearic acid at this optimum hour and temperature is 75 %. These results also verify that all the paraffin and stearic acid have been removed. Compare with the removal at 65^0C, only 72% of paraffin wax is removed at 4 hours and at 60^0C, only 61%. Besides, the microstructure analysis using FESEM image of the debinded samples proved that the paraffin wax and stearic acid have been removed by the 4^{th} hours at temperature 70^0C in comparison with the removal at first hour wax.

4.3 Thermal Debinding Results & Discussion

Figure 4.10 and 4.11 below show the results of thermal debinding for 25% Cu/MWCNTs at heating rate 3^0C/min, temperature 500^0C and dwell time 1.5 hour.

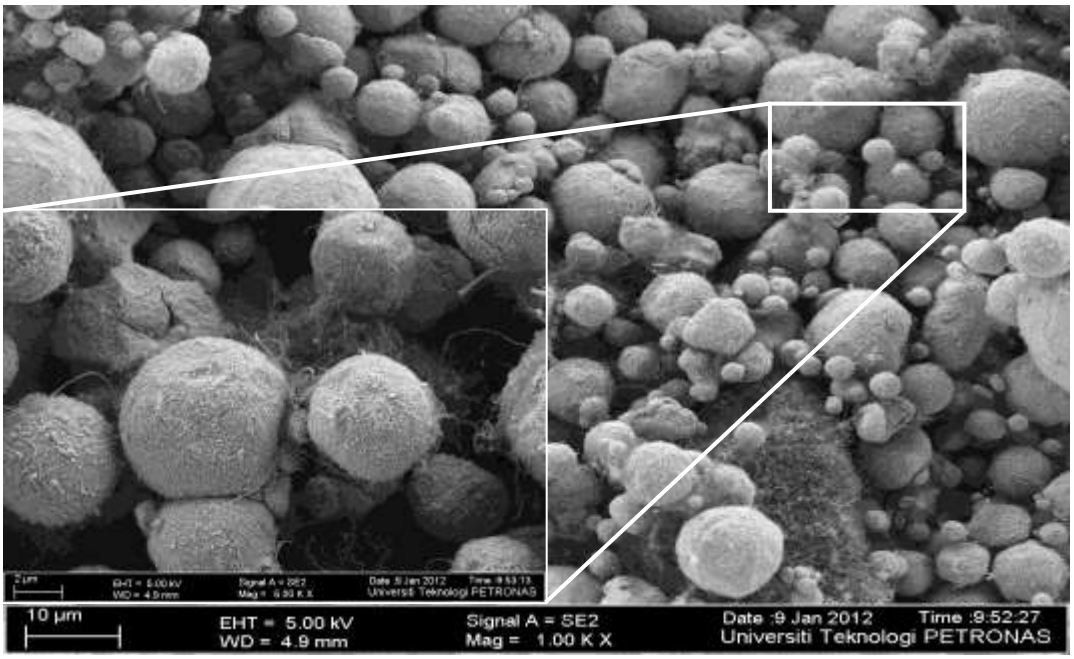

Figure 4.10: FESEM result for Thermal Debinding at heating rate 3^0C/min with 1 KX and 5 KX Mag.

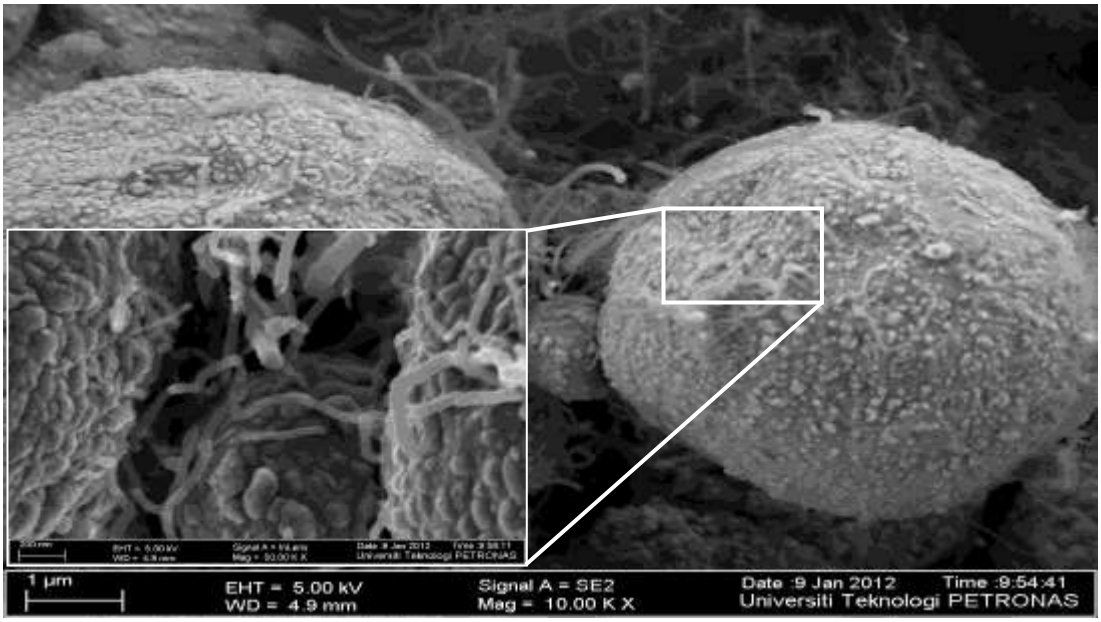

Figure 4.11: FESEM result for Thermal Debinding at heating rate 3^0C/min with 10 KX and 50 KX Mag.

Figure 4.12 and 4.13 below show the results of thermal debinding for 25% Cu/MWCNTs at heating rate 5^0C/min, temperature 500^0C and dwell time 1.5 hour.

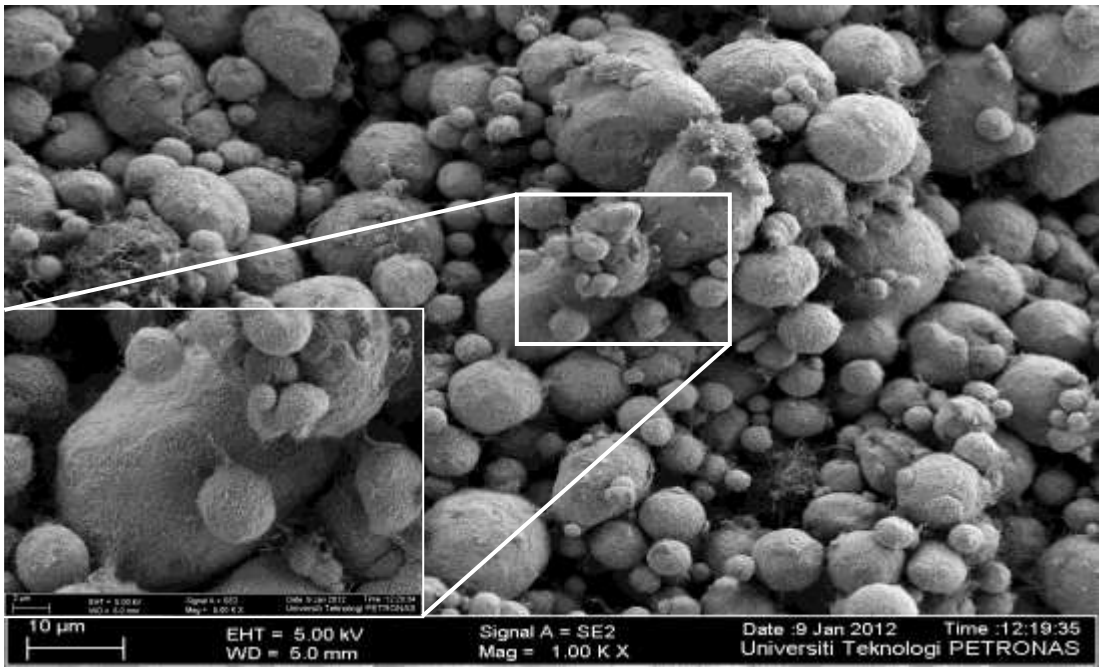

Figure 4.12: FESEM result for Thermal Debinding at heating rate 5^0C/min with 1 KX and 5 KX Mag.

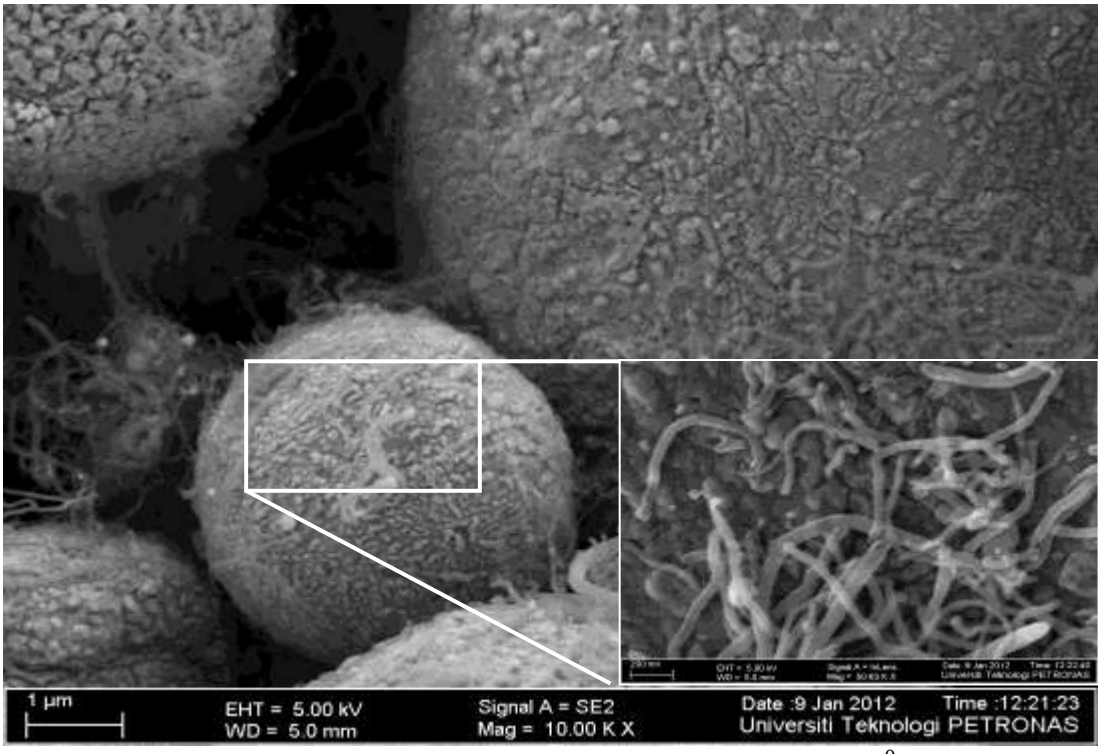

Figure 4.13: FESEM result for Thermal Debinding at heating rate 5^0C/min with 10 KX and 50 KX Mag.

Discussion

From the thermal debinding FESEM result, we can clearly see that at heating rate of 5^0C/min, there is better dispersion of MWCNTs and no more binder left. However, heating rate of 3^0C/min, also give a good result of binder removal and dispersion but our objective is to reach the maximum dispersion of MWCNTs which make heating rate 5^0C/min an optimum parameter.

4.4 Sintering Results & Discussion

Figure 4.14 and 4.15 shows the results of sintering for 25% Cu/MWCNTs at heating rate 8^0C/min, temperature 1050^0C and dwell time 1 hour and 2 hours.

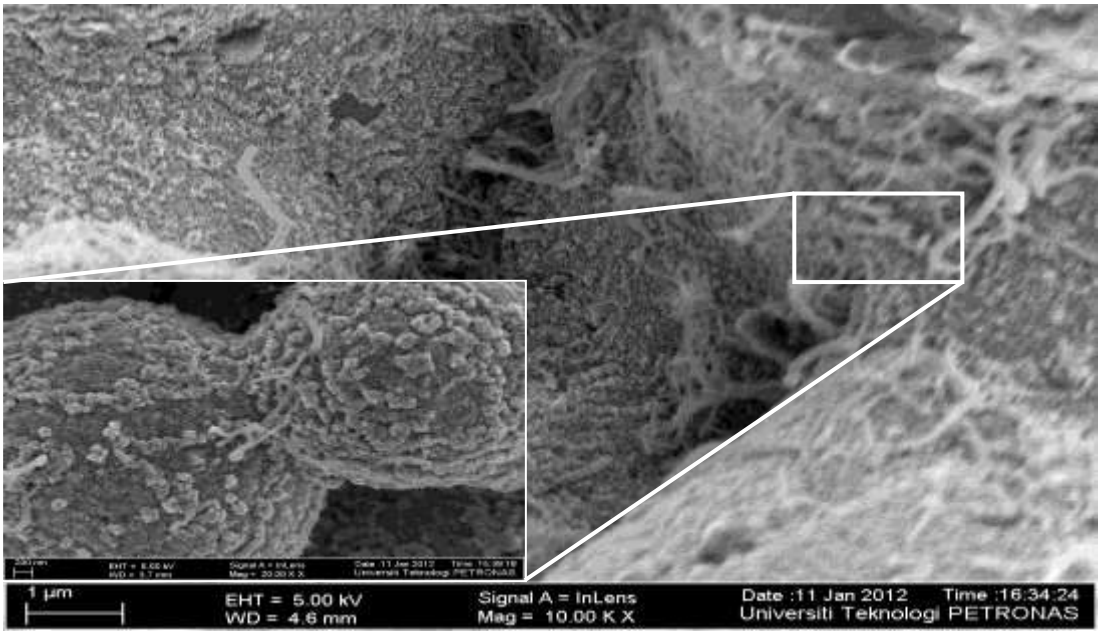

Figure 4.14: FESEM result for sintering at dwell time 1 hour with 10 KX and 20 KX Mag.

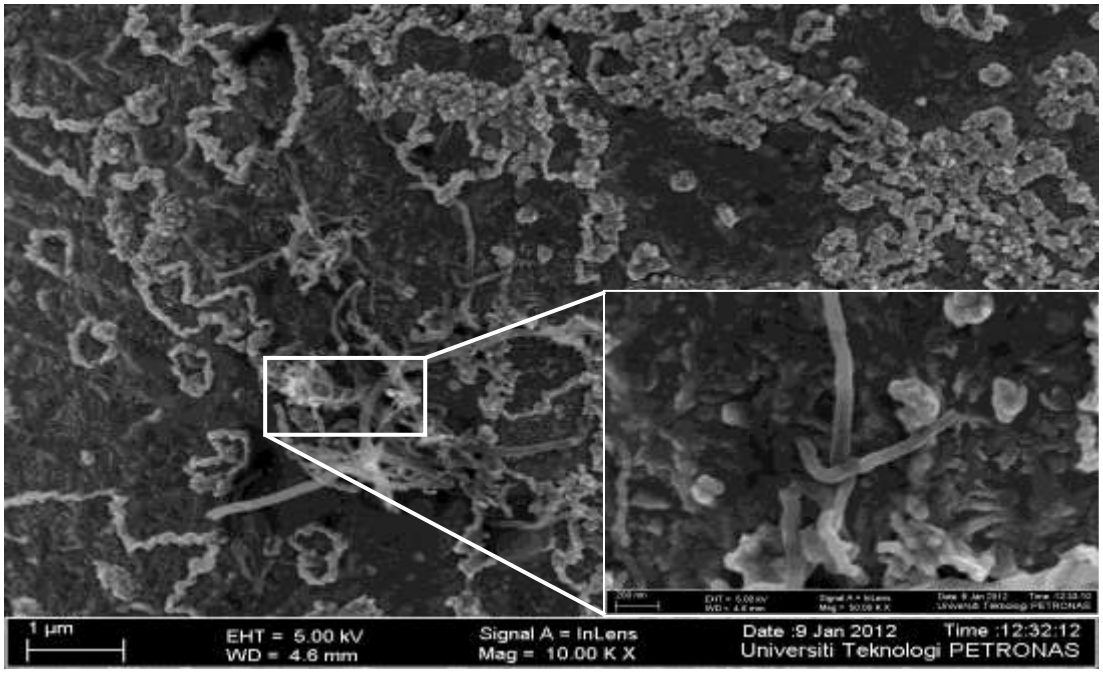

Figure 4.15: FESEM result for sintering at dwell time 2 hours with 10 KX and 50 KX Mag.

Discussion

The sintered sample at 1 hour show much more better dispersion of MWCNTs compare to the one sintered at 2 hours. From the FESEM figure 4.14 we can see that MWCNTs is dispersed all over the copper while in figure 4.15 there some portion without MWCNTs. Thus we choose dwell time 1 hour is the optimum parameter for sintering process.

CHAPTER 5

CONCLUSION

In summary, fabrication of heat sink nanocomposite material made of copper reinforced by multiwalled carbon nanotubes up to 25 Vol. % by means of powder injection molding technique has been done successfully.

In this project, a mixture of Cu-MWNTs was compounded using internal mixer machine for homogenous dispersion of the solid powder in the binder. The flow properties were measured using a capillary rheometer. To avoid binder degradation, TGA test was carried out. The TGA results showed that the processing temperature such as mixing and injection molding should be lower than 165°C. The injection molding was carried out at low pressure. A combination of solvent and thermal debinding was used for binder removal, and then the samples were isothermally sintered at an optimal sintering temperature.

Through this work, powder injection molding technique has been proved as a promising method of producing carbon nanotubes reinforced copper matrix nanocomposites efficiently. For mixing and molding stage, the optimum temperature is 160^0C. All the paraffin wax and stearic acid can be extracted by time 4 hours at temperature 70^0C. An overall dispersion of MWCNTs during sintering stage occurs at optimum parameter of 1 hour dwell time. The analysis on the morphology of MWCNTs is done using the FESEM to verify the dispersion. The development of this nanocomposite with an excellent dispersion of MWCNTs over copper can be accomplished by optimizing all the parameter at each process.

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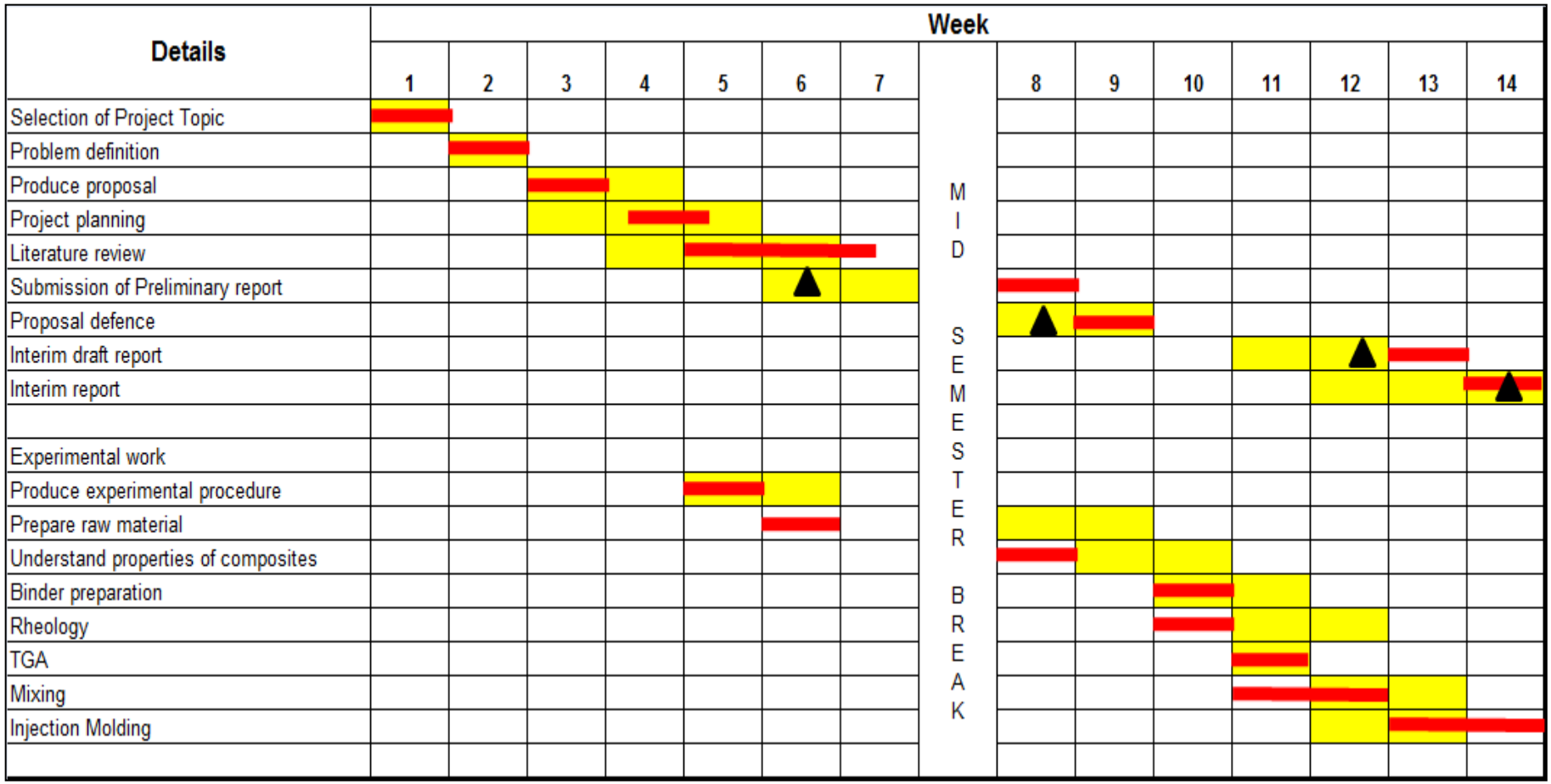
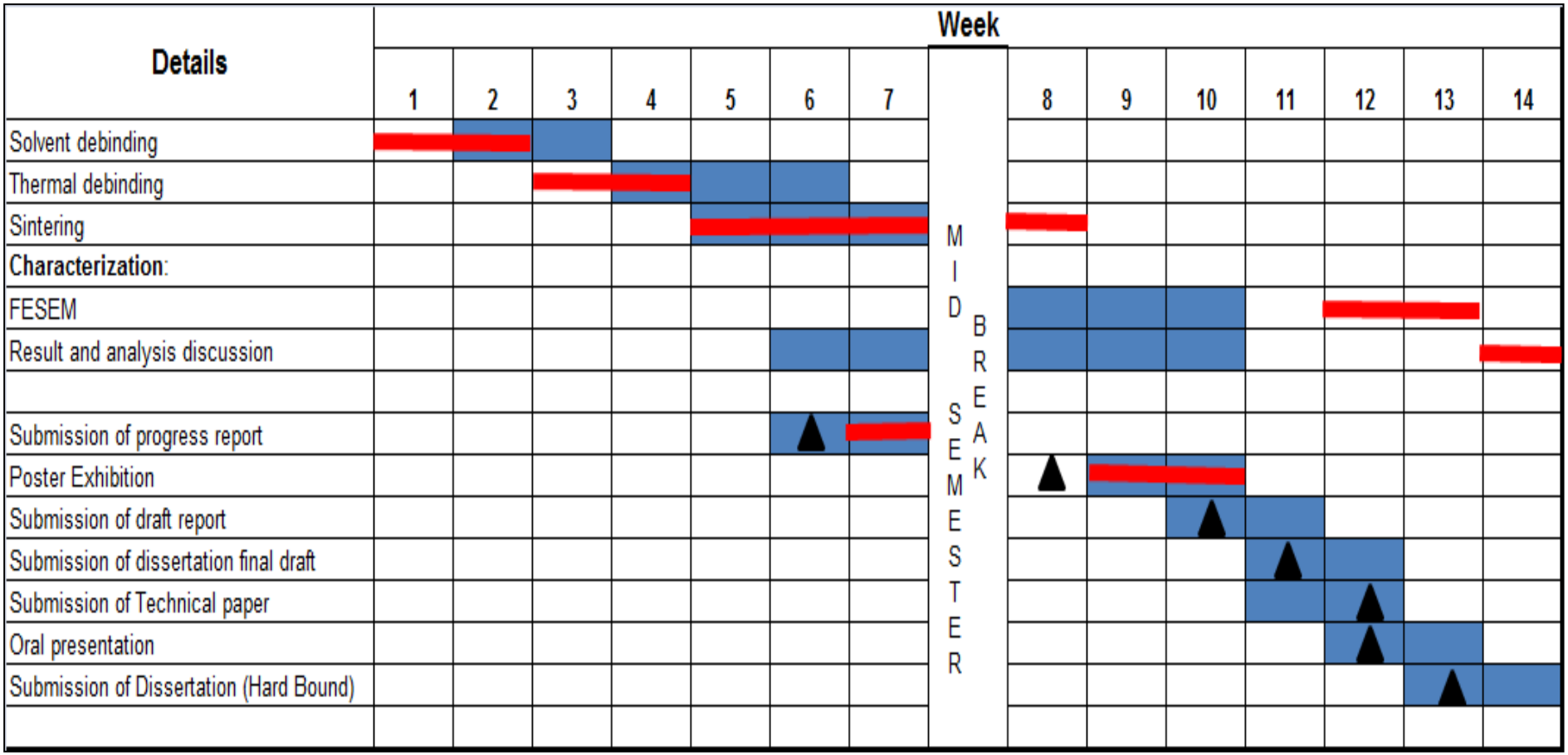
APPENDICES

Appendix A: FYP 1 Gantt Chart



: Key Milestone **: Planned** **: Actual**

Appendix B: FYP II Gantt chart



: Key Milestone : Planned : Actual