



THE PRODUCTION STUDY OF BIPOLAR PLATE FROM CUPRUM-CARBON NANOCOMPOSITE IN POLYPROPYLENE MATRIX (PP) FOR THE FUEL CELL APPLICATION

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ABSTRACT

This research is to get the parameter correlation in synthesis, micro/nano structure processes, and the candidate performance of inorganic-organic nanocomposite from the cuprum and carbon nano particles in polypropylene matrix. Besides, it also aims to get the optimal composition and evenly spread disparity/distribution from the cuprum and carbon particles in polypropylene matrix. To achieve the goals, it is conducted by two processes. The first stage includes the nanocomposite candidate fabrication with the increase of cuprum nanoparticle (0; 0, 5; 1; 1, 5; and 2 wt%) in polypropylene matrix. This cuprum nanocomposite candidate is characterized by the UV-Spectroscopy test, electrical conductivity test, the melt flow rate (MFR) test, the scanning electron microscope test (SEM), and thermal gravity analysis (TGA) test. And the second stage includes the cuprum and carbon nanocomposite candidate fabrication (5; 10; 15; and 20 wt%) with the wet chemical technique. From the research, it can be known that the cuprum nanocomposite (PP-Cu), the optimal composition is achieved in the level of nanocuprum inorganic fulfilment of 2 wt%, which it has the electrical conductivity of $9,306 \times 10^{-9}$ S/cm with the lowest band gap energy value of 3.78 eV and the highest critical temperature of 338°C also the increase of MFR value reaches 91.09 g/10 minute. Then, for the cuprum and carbon nanocomposite resulted in the second stage, the optimal composition is achieved at 20 w% of black carbon, has electrical conductivity of $5,590 \times 10^{-8}$ S/cm with the flexural modulus of 1650 MPA and also the melt flow rate (MFR) value of 16.75 g/10 minute which meet the requirement for the missal production by the moulding injection tools.

Keywords: PEM fuel cell, bipolar plate, Cu and Carbon nanocomposite, polypropylene matrix, chemistry methode.

INTRODUCTION

This paper is the result from the production research of one of the fuel cell components that is bipolar plate from the nanocomposite material with polymer matrix. This research aims to get the parameter correlation in synthesis, micro/nano structure processes, and the candidate performance of inorganic-organic nanocomposite from the cuprum and carbon nano particles in polypropylene matrix. Besides, it also aims to get the optimal composition and evenly spread disparity/distribution from the cuprum and carbon particles in polypropylene matrix.

METHODOLOGY

To achieve the goals above, it is conducted by two processes. The first stage includes the nanocomposite candidate fabrication with the increase of cuprum nanoparticle (0; 0, 5; 1; 1, 5; and 2 wt%) in polypropylene matrix. This cuprum nanocomposite candidate is characterized by the UV-Spectroscopy test, electrical conductivity test, the melt flow rate (MFR) test, the scanning electron microscope test (SEM), and thermal gravity analysis (TGA) test. And the second stage includes the cuprum and carbon nanocomposite candidate

fabrication (5; 10; 15; and 20 wt%) with the wet chemical technique.

RESULTS AND DISCUSSIONS

The test result of UV-spectro photometer

Figure-1 displays the UV-Vis reflectance spectrum result of cuprum nanocomposite sample in PP matrix with variations of 0, 0.5, 1.0, 1.5, and 2 wt%. From the figure, it can be seen that the sample reflectance level decreases along with the increase of the Cu nanoparticle fulfilment in the PP. The results in Figure-1 can be understood because visually, the sample display with nanoparticle content up to 2% has darker colour compared to the sample with lower Cu nanoparticle content or even the pure PP sample without any fulfilment particle (0 wt%). The other interesting thing which can be observed from Figure-1 is that the reflectance edge from the spectrum shifts from the low wave length to the higher one (red shift). This gives indication that the fabricated nanocomposite sample is able to give quantum effect that is the characteristic change of electronic material is in line with the decrease of particle size to the nanometer scale. This is a unique characteristic of a material system which there is a metal or semiconductor oxide inorganic material



at the nanometer range so it makes very significant the absorption side shift effect.

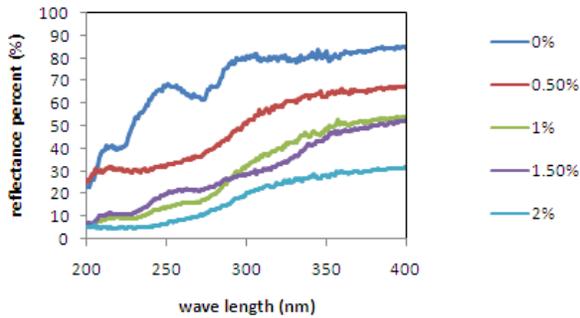


Figure-1. The Cuprum nanocomposite spectrum reflectance (Cu) with the variance of Cu inorganic phasa fulfilment level in PP matrix of 0, 0.5, 1, 1.5, and 2 wt%.

Based on the calculation using Kubelka-Munk equation, so it is obtained the absorption energy value (in eV) from the nanocomposite samples of 0, 0.5, 1, 1.5, and 2% and also the Kubelka-Munk (KM) value. While the KM value is the comparison between the quadrate from the reflectance percent remaining to the multiple value from the reflectance percent itself ($KM = [1-R]^2/2R$; R is the reflectance value). Further it can explain related to the band gap energy from the Table 1, it shows the effect indication of the cuprum nanoparticle fulfilment level in PP matrix to the KM value level.

The effect indication of the cuprum nanoparticle fulfilment level in PP matrix to the KM value level, it can be seen clearly at the determination of line tendency in each graph. Along with this, this line tendency will ease the band gap energy estimation which is the important parameter of electrical or thermal characteristics from the fabricated nanocomposite candidate. For that, before estimating the electrical and thermal characteristics in a material analysis demand, it is important to find the line equation by collecting the UV-vis measurement data.

The band gap energy is the indication of electron excitation process from the valence band to the conduction band. For this, if there is low line tendency to the energy spectrum, so the energy required by the electron for the excitation process to the conduction band is getting smaller. It means that the smaller band gap energy of a material, so the easier electron to move from the valence band to the conduction band. Related to this, the band gap energy can be determined by pulling straight line until it crosses with x-axis (the absorption energy) at each absorption energy graph to Kubelka-Munk value. By other words, the band gap energy value is the absorption energy point from a material when the KM value is zero from the straight line tendency in the absorption energy graph to the Kubelka-Munk value.

While, the band gap energy from each cuprum nanocomposite sample of 0, 0.5, 1, 1.5, and 2 wt% is shown by Table-1

Table-1. The band gap energy of cuprum nanocomposite of 0, 0.5, 1, 1.5, and 2 wt%.

The fulfilment level of Cu nanoparticle (wt%)	The band gap energy (eV)
0.0	5.80
0.5	3.81
1.0	4.38
1.5	4.47
2.0	3.78

At Table-1, it shows the value of band gap energy (eV) from the Cuprum (Cu) nanocomposite samples. This shows that in general, the bigger the fulfilment level of nanocuprum particle in PP matrix, the smaller the band gap energy from the resulted nanocomposite candidate. This can be seen from the former PP band gap energy change of 5.8 eV, after being added the Cu of 0.5 wt%, it decreases to be 3.81. It also happens when it is added with 1, 1.5, until 2 wt% of cuprum nanoparticle, the band gap energies decrease to be 4.38, 4.47 and 3.78 eV. The smaller band gap energy can be explained because if more Cu nanoparticle inputted into PP matrix, so the closer distance between clusters and this gives implication to the electron transfer from one cluster into another one, finally it gives different material conductivity value.

The electrical conductivity test result

The electrical conductivity test result to the cuprum nanocomposite candidate shows the increase of electrical conductivity in general by the increase of Cuprum nanoparticle in PP matrix. It can be understood because of the particle dispersion and continual tissue form from the conductive fulfilment material which will influence the conductivity characteristic. The interesting thing from table 2 is the electrical conductivity value of 1 wt% cuprum nanocomposite reaches the maximum value that is 1.443×10^{-7} S/cm; while the minimum value is reached 0.5 wt% of nano cuprum with the conductivity value only reaches 5.453×10^{-8} S/cm. Then, it consecutively decreases to 1.5 wt% with the value of 1.352×10^{-7} S/cm; 2 wt% with conductivity of 9.306×10^{-7} S/cm.

The tendency irregularity from the electrical conductivity value in this research is more because of the imperfection in fabrication process to the sample production for this conductivity test. This can be explained with the results from the micro structure photo by using SEM instrument, where the micro structure from cuprum nanocomposite shows the relative variance of porosity number. The enough porosity is seen at the 0.5 wt% cuprum nanocomposite, this is because of the sample production by powder method, meaning that the



nanocomposite powder gets cold compaction process then it is heated (sintering) in the oven with temperature of 200°C for one hour. It can be denied that the product characteristic from this metallurgy powder will always produce porosity. This is in line with what explain by Lenel that porosity usually happens at the compaction in compacting process.[1] While this research, 1 wt% cuprum nanocomposite shows relative small quantity and quality of porosity compared to other cuprum nanocomposite sample, meaning the number of porosity in 1wt% cuprum nanocomposite is relatively small with relatively small size compared to 0.5 wt% cuprum nanocomposite.

Callister explains that porosity is a gas or air trapped in material micro structure. The porosity will influence the mechanical and electrical characteristics from polymer matrix composite. In general, the porous structure will cause the decrease of mechanical characteristic if compared to more solid structure. Further, Callister explains, porosity also strongly decreases the electrical conductivity because it will obstruct the electron flow movement transmitting the electrical energy. [2] In line with this, Lenel explains that the porosity will be caused by the shrinkage or by trapped gas. The shrinkage happens at compaction in the compacting process.[1] And due to the material transmission as the main source of porosity formation, this is resulted from the volume decrease followed by the compaction due to compaction by the compacting. While, the porosity by the gas, it is resulted in from the temperature change in material micro structure.

Test results of thermal gravimetry analysis (TGA)

The test results of TGA, it is gained weight percent ratio with temperature. In this study, it shows the extent of drastic weight loss in specified temperature range. The weight loss is started by a decrease in the weight percentage of cuprum nanocomposite. The weight percent loss of 1 wt% cuprum nanocomposite at 351°C temperature reaching 0.98%, is indicated by the remaining percent weight which is equal to 99.02%. The weight loss percent of 1.5 wt% cuprum nanocomposite loss at 351°C temperature is 0.94%, because the remaining weight percent is 99.04%. As for the 2 wt% cuprum nanocomposite, the weight loss at temperature of 391°C is

1%. This is indicated by the remaining percent weight of 99% on.

In addition to the above, the important information that can be retrieved from the TGA test is the temperature at which it starts to lose the weight of each cuprum nanocomposite of 0.5, 1, 1.5 and 2 wt%. The results show that 0.5 wt% nanocomposite starts to lose weight at a temperature of 234°C. While, the temperatures to start to lose weight for each cuprum nanocomposite of 1, 1.5, and 2 wt% are 269, 234, and 338°C.

The temperature at which it starts to lose weight from a polymer matrix composite material; it can be important information to estimate the thermal properties of materials. This is reasonable because in the fuel cell applications, these materials will get thermal stress due to the operating temperature. Especially for PEM fuel cells, a bipolar plate should have heat stability up to a temperature of 1200C. [3] While the results of this study indicate that the lowest temperature of the nanocomposite cuprum for weight loss of 234°C is 0.5 wt% percent charge of nano cuprum. In contrast, the highest temperature is achieved at 2 wt% nano cuprum percent charge with the value 338°C. This can be explained due to the higher filling level of nano cuprum, there will be a barrier to the flow movement of the PP matrix decomposed by heat. And this can be explained by the results research by Scholta J at al that combines graphite with thermoset resins which indicates stable temperature stability. [4]

The test results of melt flow rate (MFR)

MFR testing is needed to determine the flow characteristics of nanocomposite cuprum candidate. These characteristics can be attributed to the ability of the nanocomposite to be produced in large quantities (mass). It is strongly associated with the commercialization of the bipolar plate from the nanocomposite material, using injection molding method. In addition, the MFR value indicates the ability of a material to fill in the smallest and farthest part in a mold. This means, the greater the MFR value of a material, then the better the ability to form a thin and complex geometry. The other way around, the smaller the MFR value, it will be very difficult melt flow to fill the material in the smallest and farthest part in the mold.

Table-2. The Test results of melt flow rate (MFR) nanocomposite of 0.5,1, 1.5, and 2 wt%.

The composite candidate	0 %	0.5 %	1 %	1.5 %	2 %
MFR (gram/10minute)	28.5	35.31	35.0	43.7	91.0

Related to the things above, the minimum value of MFR whiis commonly used in the industry as a requirement for mass production by means of injection molding is 10 g / 10 min. [5] From the MFR test, it is obtained the results showing that the nanocomposite sample of cuprum get increasing MRF value when the

composition of nano cuprum is increased. The successive of MFR values of cuprum nanocomposite from percent fulfillment of 0.5, 1, 1.5, and 2 wt% is 28.51 g / 10 min; 35.31 g / 10 min; 35.05 g / 10 min; 43.72 g / 10 min; and 91.09 g / 10 min.



This study shows that the greater the percentage of nano cuprum added in the polypropylene matrix, the more it will increase the melt flow rate of cuprum nanocomposite. It can be explained that the addition of cuprum also helps the process of lubrication or sliding in the PP material. So that when the PP starts to be degraded and composed, the cuprum nanoparticle also gives contribution to accelerate the sliding. This is in line with the research function of graphite by Robberg *et al* making the bipolar plates with a combination of graphite and polymer resin by compression molding method. Robberg explains that graphite can help simplify the process of compression molding due to the lubrication effect at

melting process. [3] As a result, the viscosity level of the melt becomes low due to so big and fast formation of molten PP. By this low viscosity, so the PP melt flow rate is higher. At the end, it will affect the melt flow rate per unit time.

The electrical conductivity test result of cuprum and carbon nanocomposite

The average electrical conductivity value of bipolar plate composite candidate sample in this research can be seen in Table-3.

Table-3. The average electrical conductivity value of cuprum and carbon composite candidate with black carbon fulfillment variance of 5, 10, 15, and 20 wt%.

Sample	5% CB	10% CB	15%CB	20%CB
Conductivity (S/cm)	2.447E-08	2.947E-08	5.389E-08	5.590E-08

In Table-3, it shows the increase value of the average electrical conductivity (S / cm) on cuprum and carbon nanocomposite with the addition of organic phase (carbon black) in the PP matrix. This is understandable because the carbon black has a high conductivity value (about 10² ~ 10⁵ S / cm). The addition of conductive filler particles will change the final properties of the composite, where the previous PP insulator (conductivity of about 10⁻¹⁴ ~ 10⁻¹⁷ S / cm) has increased significantly with the addition of conductive carbon black particles. This can be explained by the concept of "percolation threshold" proposed by Clingerman *et al* which describes how the electrical conductivity of a polymer-carbon composite material in general is significantly affected by the fulfillment fraction volume. At low levels of fulfillment, the electrical conductivity of the composite is still low and very close to the value of insulator polymer. But at a critical point or range, the electrical conductivity increases very sharply with the increase in the small proportion of conductive filler material. This range or point is what called as "percolation threshold". The conductivity continues to significantly increase until it reaches saturation point which is the intrinsic conductivity value that is owned by a conductive filler material. Clingerman *et al* also report that the characteristics of carbon fillers such as the type, size and shape of the

particles determine the percolation threshold and the conductivity of the composite. [6]

The MFR test results of cuprum and carbon nanocomposite

The MFR value of cuprum and carbon nanocomposite candidates that tend to decrease when the percentage of carbon black in the PP matrix is increased. The successive MFR values of nanocomposite candidate with inorganic phase fulfillment levels of black carbon, 5 wt%; 10 wt%; 15 wt%; and 20 wt% is 22.73 g / 10 min; 20.92 g / 10 min; 17.57 g / 10 min; and 16.75 g / 10 min. This decrease of MFR value is because the addition of carbon black particles adding pin or barrier in the PP flow movement which has melted. This is similar to Zweifel, which states that the coefficient value of the fiber linear thermal expansion is negative. Consequently, there is a high viscosity due to the black carbon does not come melted and actually impede the PP flow. Thus, as a result of 'locking' the PP flow movement causes the MFR value of cuprum and carbon nanocomposite becomes low. [7]

The test result results of cuprum and carbon nanocomposite flexural

At Table-4, it shows the test results of cuprum and carbon nanocomposite with fulfillment level variance of 5, 10, 15 and 20 wt% black carbon inorganic.

Table-4. The test results of cuprum and carbon nanocomposite with fulfillment level variance of 5, 10, 15 and 20 wt% black carbon inorganic.

Percent of black carbon	5 %	10 %	15 %	20 %
The Flexural Modulus (MPa)	1120	1140	1000	1560
The deviation Standard (s)	495	808	85.3	574
Variance / Variety (v)	40.44	71.12	8.52	36.72



In Table-4, it shows the addition effect of carbon black in some degree of variation to the flexural modulus of the cuprum and carbon nanocomposite. The decrease of flexural modulus is from PP, which originally reaches 1260 MPa. This decrease occurs at 5 wt%, 1 wt% and 15 wt% of filling variations. However, there is an increase in 20 wt% carbon black percentage to reach 1560 MPa. In addition, the addition of carbon black per cent until 15 wt% has no effect on the increase of flexural strength for 5 ~ 15 wt% carbon black which are added (indicated by the flexural modulus) on cuprum and carbon nanocomposite in this study. It is seen from the flexural modulus values for 5 ~ 15 wt% carbon black which is added showing the 'similar' downward trend (1120 MPa, 1140 MPa and 1000 MPa). This means, to increase the flexural strength of cuprum and carbon nanokompisit, it needs to add at least 20 wt% of organic carbon black in the PP matrix. This is in line with the opinion of Mighri, stating that the addition of carbon black and graphite for approximately 30-70% is useful to increase the strength of composite materials and also to obtain a low resistivity (about 10-3-10-2 Ohm.cm). Thus, the black carbon will significantly influence when its addition percentage in the polymer matrix is at least 20%. [8]

The tensile strength test results of cuprum and carbon nanocomposite

The Tensile Strength test results from cuprum and carbon nanocomposite can be seen in Figure-2.

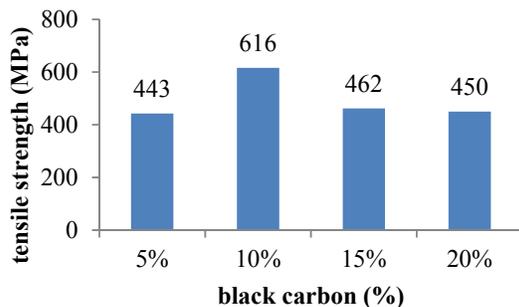


Figure-2. The tensile strength test results (MPa) of cuprum and carbon composite with fulfillment variance level of 5 wt%; 10 wt%; 15 wt%; dan 20 wt% black carbon organic phase.

In Figure-2, it shows the tensile strength of cuprum and carbon nanocomposite candidates. It shows the successive values of nanocomposite candidate tensile strength with fulfillment variation of inorganic carbon black phase of 5 wt%; 10 wt%; 15 wt%; and 20 wt%. From Figure-2, it is seen that the cuprum and carbon nanocomposite with 10 wt% percentage rate reaches the highest value that is 616 MPa. This is due to the synergy of three filler, namely cuprum, carbon black, and carbon fiber which works very optimal. This is consistent with the

conclusions Wang, in his research that the composite with three fillers gives better results than the composite with one or two fillers. [9] [Wang Y: 2006] Another supporting explanation is that can be seen from the TGA test results, providing information about good temperature stability at 2 wt% nano cuprum fulfillment level on a single nanocomposite filler. However, too big addition of carbon black will eliminate the synergy power with other fillers. This can be seen from the addition of carbon black percentage up to level of 15 and 20 wt%, which even decreases the tensile strength of cuprum and carbon nanocomposite candidates to 462 and 450 MPa. Thus, the addition of carbon black after passing the point of optimum synergy does not influence the tensile strength of cuprum and carbon nanocomposite. This is indicated by the value of the tensile strength which tends to be almost similar ranging at 450 MPa.

Summary

This research results in several conclusions, namely:

1. Fabrication of first stage fabrication result of cuprum nanocomposite, gives a positive indication on the change in the electronic properties with the addition of nanocuprum in the polypropylene matrix. The cuprum and carbon nanocomposite produced in the second stage, shows a consistent increase of conductivity value by the addition of carbon black.
2. The optimum composition for the nanocomposite fabrication as a fuel cell material with wet chemical method can be divided into two parts:
 - a. The first stage fabrication which produces cuprum nanocomposite, the optimum composition is achieved at the level of inorganic nanotembaga fulfillment of 2 wt%. In this composition, the band gap energy value reaches a minimum point up to 3.78 eV.
 - b. For cuprum and carbon nanocomposite produced in the second stage, the optimum composition is achieved at 20 wt%. This is shown by the results of flexural testing where the highest flexural modulus value reaching 1560 MPa. Apart from that, the conductivity test results place 20 wt% nanocomposite to be the best composition compared to other compositions (5, 10, and 15%)

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