

## The Effect of Argon and Liquefied Petroleum Gas Ratio on The Properties of The Diamond-Like Carbon on The Surface of 316L Stainless Steel

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### Abstract

316L Stainless steel (SS 316L) is a metal material that has superior corrosion resistance properties, so this material is widely used in medical, manufacturing, nuclear, food, etc. However, this metal can still be damaged or scratched due to weaknesses in hardness and wear resistance. This research was carried out to overcome these shortcomings by using Diamond Like Carbon (DLC) coating which can improve the hardness and wear resistance of SS 316L. DLC coating was done using the glow discharge plasma technique at temperature of 400°C and pressure of 1.6 mbar for 4 hours with variety of argon (Ar) and LPG gas mixtures. The results of DLC coating optimum conditions were obtained at the gas mixture ratio of 80% Ar and 20% LPG with the increase of hardness from 157.9 VHN to 329.84 VHN, and wear resistance decreased from  $1.0176 \times 10^{-3}$  mm<sup>3</sup>/kg.mm to  $0.7 \times 10^{-3}$  mm<sup>3</sup>/kg.mm. The improvement in the properties of this treatment was proven by SEM EDS which showed the formation of 69% graphite phase (G) and 31% diamond phase (D), as well as from Raman spectroscopy analysis, sp<sup>3</sup> and sp<sup>2</sup> bonds were obtained.

**Keywords:** 316L Stainless steel; Diamond Like Carbon (DLC); Hardness; Wear resistance

### 1. Introduction

Material selection is very important in the engineering field, which the properties of the material used must be appropriate to its use[1]. Stainless steel is a steel alloy with the addition of chromium so that the material is resistant to rust[2]. Based on the composition and percentage content of Cr-Ni, stainless steel is divided into martensitic, ferritic, austenitic, and duplex [3]. 316L stainless steel (SS 316L) is a type of austenitic stainless steel which comes from a mixture of Fe, Cr, Ni[4]. This material has a low carbon content so its resistance to corrosion is very strong so it is widely used in research for use in various industries. SS 316L is used in researches for artificial joint [5], bone tissue regeneration[6], orthopedic[7], orthodontic[8], etc. Many studies have been conducted to analyze the use of SS316L pipes[9] and valves[10] components. SS 316 L is a basic shielding material used to reduce the effects of exposure to nuclear radiation[11][12]. Because SS 316L is food grade, many studies have used this material as a component in food processing and storage using SS316L[13][14].

However, despite its benefits and advantages, SS 316L has relatively low hardness[15] and wear resistance[16], so that its implementation requires special treatment on the surface to improve the properties of this material. To overcome this weakness, DLC surface coating treatment was carried out. The coating process is carried out using the plasma glow discharge chemical vapor deposition (CVD) technique, which is chemical coating process on the substrate surface that occurs due to the interaction of energetic ions. The advantages of CVD (Chemical Vapor Deposition) are that the resulting coating

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has high hardness and good wear resistance[17]. The formation of DLC on metal surfaces generally uses a mixture of hydrocarbons with Ar plasma such as Ar with CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, or C<sub>2</sub>H<sub>4</sub>. Because the price is expensive, this research uses LPG as a carbon source, which is a mixture of propane (C<sub>3</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>), and the rest is hydrocarbons such as ethane (C<sub>2</sub>H<sub>6</sub>) and pentane (C<sub>5</sub>H<sub>12</sub>) as well as other contamination at very low levels[18][19].

To make thin layer of Diamond Like Carbon using the glow discharge plasma technique requires[20], hydrocarbon gas[21] which can be taken from LPG gas which is then injected into a plasma tube. The workpiece which is placed on the cathode will be deposited onto the surface of the substrate. Plasma is the fourth physical state after solid, liquid and gas. Plasma can be formed by ionizing gas through an electric discharge in a low-pressure tube, laser heating, direct current (DC) sources, and microwave fields[22]. The deposition technique is a technique used to deposit ions (plasma) on an object to form a plasma layer. There are several techniques for creating layers; evaporation technique (vacuum evaporation), ion beam sputtering technique, and glow discharge plasma technique.

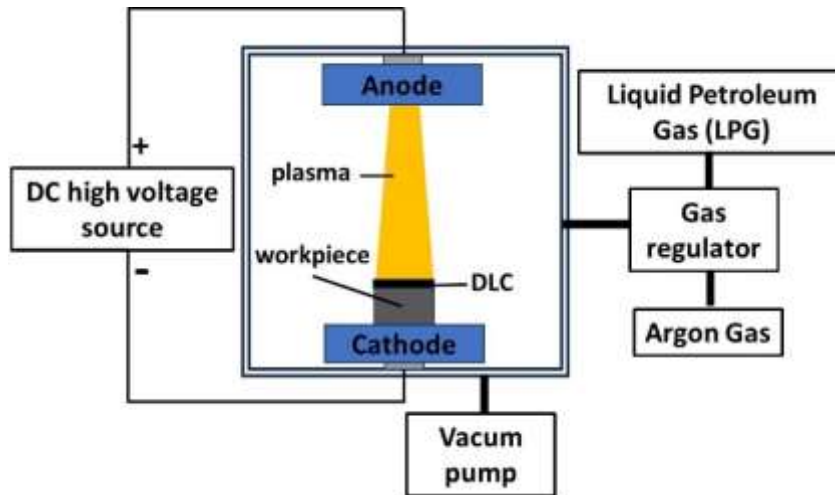
Previous research was conducted on the Effect of CVD Plasma Post Treatment of DLC Coating on the Surface Hardness Properties of AISI 410 Steel by Anhar et al. This research was carried out by thin layer deposition by CVD plasma using a mixture of Ar, CH<sub>4</sub>, and He. The pressure, temperature, and time used were 1.6 mbar, 300°C, and 4 hours respectively, and varying times of 10 - 30 minutes. This process can increase the hardness of AISI 410 from 232.3 VHN to 301.2 VHN[23]. Another research was carried out on the effect of changes in DC glow discharge plasma nitriding temperature on the hardness of AISI 4140 steel. The tests carried out were related to material hardness, microstructure testing after the plasma nitriding process. Plasma nitriding on the surface of steel with varying temperatures has been proven to increase hardness by up to 51.5%, namely from 97.8 VHN to 189,975 VHN[24]. Sujitno et al, conducted research entitled Effect of Diamond-Like Carbon Thin Film on the Fatigue Strength of AISI 4340 Steel. This research explains the effect of DLC coating applied to the surface of AISI 4340 steel using the CVD technique. The DLC coating process uses a mixture of argon (Ar) and methane (CH<sub>4</sub>) gas with a ratio of 24%: 76%, temperature 400°C, various gas pressure variations (1.2 mbar, 1.4 mbar, 1.6 mbar, 1.8 mbar, and 2.0 mbar) and a coating time of 5 hours, resulted in an increase in fatigue strength from 401 MPa to 514 MPa, microhardness from 327 VHN to 625 VHN[25].

This research was conducted to investigate the effect of variations in the composition of the Ar and LPG gas mixture in the DLC coating process on the mechanical properties and chemical bond structure of 316L stainless steel material resulting from DLC coating. After DLC coating is carried out, it is hoped that there will be an increase in the mechanical properties of SS 316L in order to meet the biocompatible material requirements. Therefore, hardness, roughness, wear tests were carried out, as well as SEM-EDX analysis, Raman spectroscopy and x-ray diffraction.

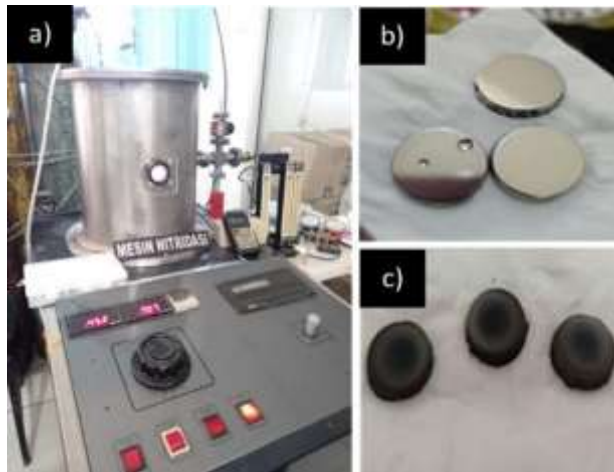
## **2. Research Methodology**

The research materials used were SS 316L plate cut into disc-shaped samples with diameter of 15 mm and thickness of 3 mm. Sandpaper was used to smooth the surface from debris remaining during the cutting process. Argon gas and LPG as a carbon source to form the thin layer of DLC. Autosol is used to polish the samples surface till shiny like a mirror. 70% alcohol, soap, and water is used to clean the sample from dirt on the surface. Tissue is used to dry the sample surface after cleaning and to wrap the sample to protect it from scratches. Closed containers and silica gel are useful for storing and keeping samples in a dry condition. The process begins with sample preparation which begins by making a disc-shaped sample with a predetermined size, until it is cleaned from all contamination.

The DLC deposition process was carried out for 4 hours with a pressure of 1.6 mbar and the temperature maintained at 400°C. Samples that have been coated and those without coating are subjected to mechanical property characterization tests, especially for hardness and wear resistance. Figure 1 describes the setup of equipment of discharge plasma for coating the surface of SS 316L in this study.



**Figure 1.** Schematic of the Plasma Discharge Equipment



**Figure 2.** a) Equipment for deposition, b) Samples of SS 316L before deposition, c) Sample of SS 316L after deposition

The samples used in this research were SS 316L without the deposition process (Sample A) and the samples carried out the deposition process with Ar : LPG ratios of 90:10 (Sample B), 85:15 (Sample C), 80:20 (Sample D), 75:25 (Sample E). One of the samples will be analyzed by observing micro characterization using SEM-EDX, XRD and Raman spectroscopy. Figure 2a is Equipment for deposition, Figure 2b is the sample of SS 316L before deposition, and Figure 2c shows the SS 316L after deposition.

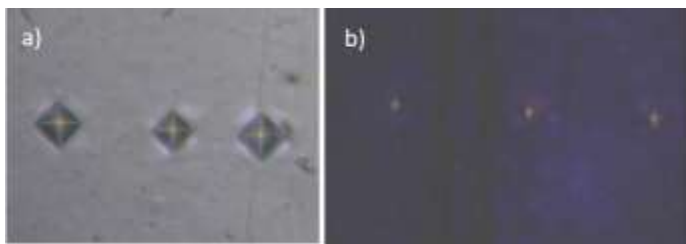
### 3. Results and discussion

In this research, Diamond Like Carbon (DLC) layer deposition process has been carried out on the SS 316L substrate using the glow discharge plasma technique. Glow discharge plasma is a method of generating plasma with an electric discharge, where the test sample is placed between a high voltage electrode (cathode) and a neutral electrode (anode) in a reactor tube that is connected to an electric current power generation source. The hardness test was carried out on the surface with an indenter load of 10 gf with an indentation time of 10 seconds at 5 different points to obtain an average hardness for each sample. The Vickers hardness test are shown in Figure 3a and Figure 3b.

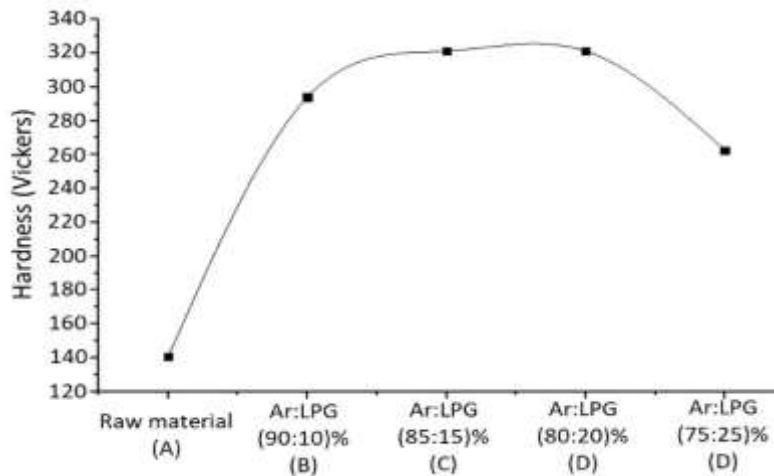
Figure 4 shows the hardness of the samples used in this study, and Figure 5 shows the wear resistance of the samples. It can be seen that there was a decrease in the wear resistance value of the SS 316L material after being coated with DLC. In explaining the hardness value and wear value are inversely proportional, which the higher the hardness value, the lower the wear resistance value, so the longer the service life. It can be concluded that the denser the carbon composition deposited on the SS 316L material, the harder the surface and the lower the wear resistance value.

After mechanical testing, it was found that the optimum composition of Ar ; LPG was 80:20 (Sample D), so further characteristics were carried out to determine the influence of the material's microscopic properties on its mechanical properties. Scanning Electron Microscopy-Energy Dispersive X-ray spectroscopy analysis has been carried out on Sample D at a voltage of 20kV with a magnification of 5,000 times. The purpose of this test is to determine the relationship between surface morphology and elemental composition with the mechanical properties of the material such as hardness,

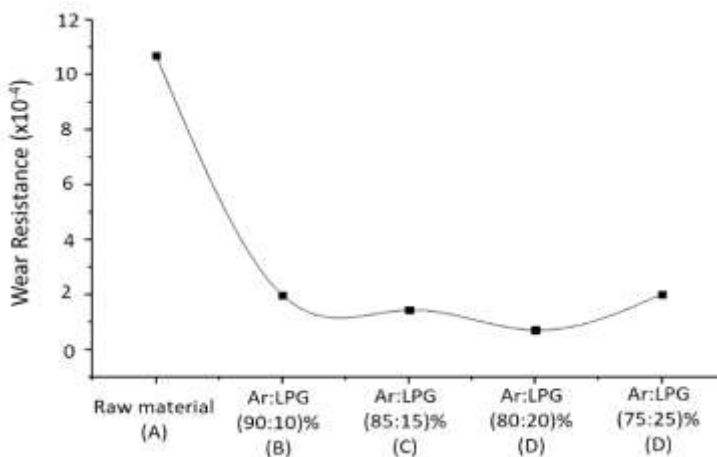
The SEM-EDX test results shown in Figure 6. In the appearance of the microstructure of sample D, the morphological structure of the sample surface appears to be textured with few crystal defects, but it does not look very sharp. The results of elemental composition analysis using EDX also show an increase in carbon elements combined with FeNiCr elements. In this image, the crystal defects formed are traces of the results of the glow discharge energy during the implant process. According to Sudjatmoko et al (2013), the ion implantation process can form a layer of new elements on the surface[26]. This layer influences the characteristics of the implantation sample.



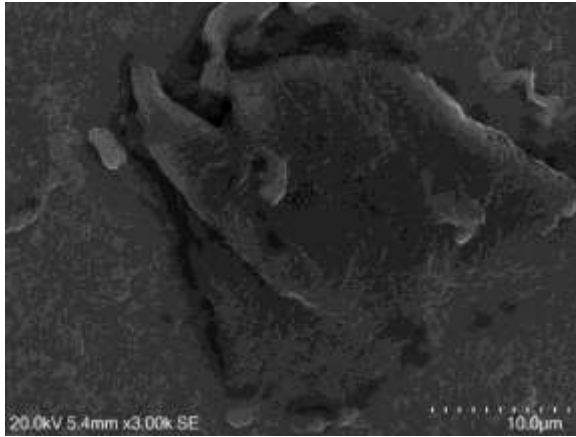
**Figure 3.** Image of hardness testing on SS316, a) Sample before deposition, b) Sample after deposition



**Figure 4.** Hardness of raw materials of SS 316L and SS 316L that have been deposited

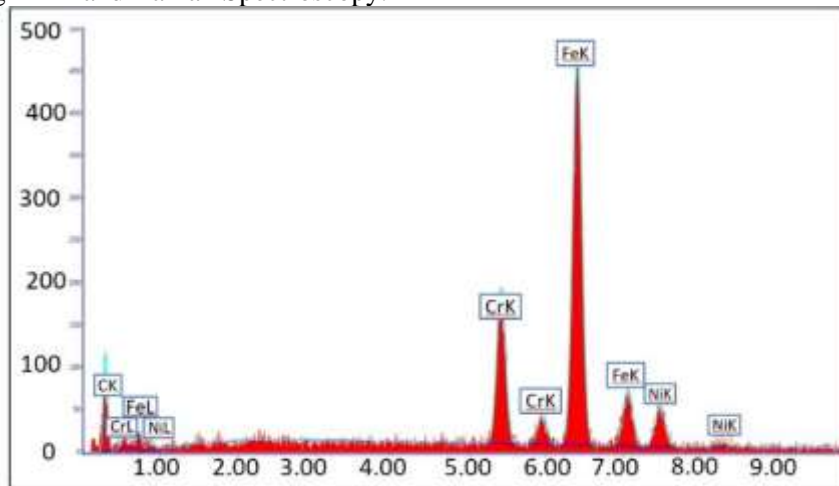


**Figure 5.** Wear resistance of raw materials SS316L and SS 316L that have been deposited

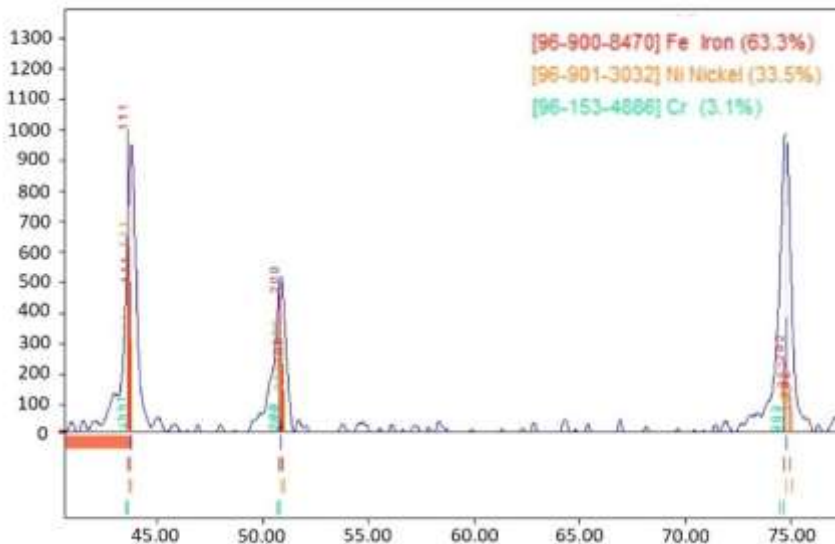


**Figure 6.** SEM image of the surface of the SS 316L deposit with the Ar 80% and LPG 20%

In the SEM-EDX test (Figure 7), it can only prove the presence of carbon content after implantation, but cannot prove the presence of a carbon layer and what bonds are formed on the surface layer. The crystal defects formed on the surface layer of Sample D do not necessarily indicate the formation of DLC layer because this could have occurred because the 316L stainless steel casting process was not homogeneous on the surface. The carbon layer and bonds formed on the surface of SS 316L can be proven accurately using XRD and Raman Spectroscopy.



**Figure 7.** Spectrum from XRD test of SS 316L deposit with the Ar 80% and LPG 20%

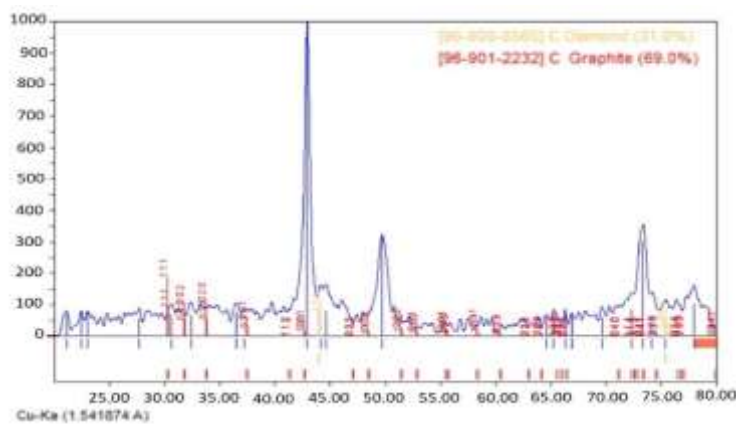
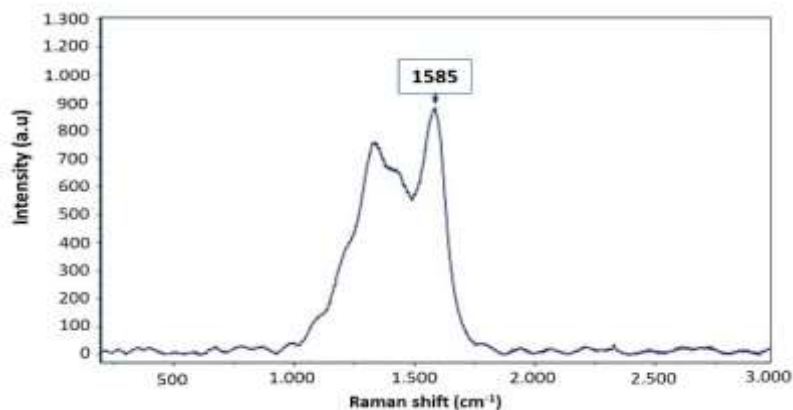


**Figure 8.** Spectrum from XRD test of SS 316L deposit with the Ar 80% and LPG 20%

To prove the phase and see the presence of a DLC layer after the glow discharge plasma deposition process on the SS 316L substrate, X-Ray Diffraction analysis was carried out using Cu-K $\alpha$  X-ray radiation source with a wavelength of 1.54187Å. This test was carried out on 2 samples, sample A (without deposition treatment) and sample D (optimal value in the hardness test). The XRD test results were analyzed using the COD (Crystallography Open Database) database contained in the Match3 program.

Based on the diffraction pattern formed in Figure 8, it shows that in sample A (raw material) there are three main elements detected, namely index A entry number 96-900-8470 which is a database of Fe (iron) 63.3% which is shown by the colored line red, index B entry number 96-901-3032 which is database of Ni (nickel) 33.5% which is shown by the orange line, and index C entry number 96-153-4886 which is a database of Cr (chromium) 3.1% which is shown by the green line. Meanwhile, the diffractogram results for sample D, DLC treatment of glow discharge plasma with a percentage of Ar (80%) : LPG (10%) are shown in Figure 9. It shows that the phases formed are index A entry number 96-900-8565 which is the database of the Diamond (C) 31.0% phase which is shown by the yellow line and index B entry number 96-901-2232 which is database of the 69.0% Graphite (C) phase shown by the red line. From the results of this analysis, it can be seen that the layer formed is really a DLC layer composed of Diamond (C) and Graphite (C) phases.

Figure 10 shows the contribution of graphite is greater than diamond, where this result is in accordance with the next analysis, namely in the discussion of Raman spectroscopy. The existence of indications that have been proven by previous mechanical tests on SS 316L samples with DLC glow discharge plasma deposition treatment, was then verified using Raman Spectroscopy analysis to determine the dominance of sp<sup>2</sup> (graphite) and sp<sup>3</sup> (diamond) bonds. From Figure 10, it can be seen that the sp<sup>2</sup> (graphite) value is 1,585.55 cm<sup>-1</sup> with estimated peak intensity of 880 counts and the sp<sup>3</sup> (diamond) value is  $\pm$ 1,350 cm<sup>-1</sup> with estimated peak intensity of 762 counts.

**Figure 9.** The XRD spectrum of the Ar 80% and LPG 20% that shows the presence of diamond phase

**Figure 10.** The spectrum from Raman Spectroscopy on the Ar 80% and LPG 20% shows the presence of diamond phase

The results obtained in this study showed a trend of DLC hardness that was almost the same as previous studies, the difference between this study and previous studies lies in the process parameters. Which in the study of Sudjatmoko, et.al.[26], it was used variations in implantation energy, and in the study conducted by Tjipto Sujitno[25], et.al., it was used variations in the gas pressure. In general, the presence of DLC on the surface of the material will increase the hardness, which will then increase the wear resistance of the material. Raman spectroscopy is used to determine the presence of certain materials on the surface[27], and the presence of DLC layer, it is indicated by the results of raman spectroscopy, which is not shown in the two studies conducted by Sudjatmoko, et.al and Tjipto Sujitno, et. al.

#### 4. Conclusions

The formation of the graphite and diamond (DLC) phase is what causes the hardness to increase and the wear rate to decrease. The optimum conditions of Ar:LPG gas ratio is 80:20, which it can increase the hardness from 157.9 VHN (raw material) to 329.84 VHN, and wear rate decreases from  $1.0176 \times 10^{-3}$  mm<sup>3</sup>/kg.mm to  $0.7 \times 10^{-3}$  mm<sup>3</sup>/kgmm. Raman spectroscopy shows the types of bonds formed were SP<sup>3</sup> and SP<sup>2</sup>, these results are shown by the peaks of D (diamond) and G (graphite) which are respectively shown at a wave length shift of around 1,350 cm<sup>-1</sup> and 1,585 cm<sup>-1</sup>. Also from XRD analysis, the results showed that the phases formed were graphite phase (G, 69%) and diamond phase (D, 31%), and from SEM-EDS analysis, carbon element content of 38.8% was detected. These results indicate that there is a match between the results of Raman, XRD and SEM-EDS analysis.

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