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Synthesis of Crumpled Graphene by Fast Cooling Method

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Abstract. Graphene nanoflakes can be corrugated into three other different structures such as rippled, wrinkled and crumpled graphene. Among the three types of corrugation, crumpled graphene has the most suitable surface topography as well as the largest active surface area for enhancement through attachment with other nanoparticles. Even though crumpled graphene has been widely used, its production operating parameters are still not optimized. With the existence of multiple methods and procedure introduced to produce a crumpled graphene, each research also suggested varying operating condition for the synthesis of crumpled graphene. The focus of this research is to investigate the effect of temperature lower than 0°C on the surface morphology and topology of a graphene nanoflakes. Powdered graphene nanoflakes is synthesized by using the fast cooling method to produce crumpled graphene. The temperature was varied between -20°C, -40°C and -80°C. The process is followed by chilling at -20°C for 24 hours and later centrifugation of melted samples of graphene from distilled water. The sample analysis is carried by using SEM to study the structural morphology of the crumpling degree on the graphene surface and EDX used to determine the chemical composition of the sample. TGA to determine the degradation temperature of the sample, if there is any significance effect when compared to the natural graphene nanoflakes and finally the sample is tested with FTIR to determine the functional group and bonding which existed in the prepared samples. The obtained result indicated that higher degree of crumpling occurs when the graphene is exposed to a much lower temperature. The SEM images indicates that more crumpling occur on the single nanoflakes when freeze to -80°C compared to freezing at -40 and -20°C. There is a positive relation between the low temperature method and the crumpling degree of the graphene nanoflakes. The composition of graphene even after corrugation using fast cooling method remain the same and the degradation temperature does not deviate as much after crumpling.

INTRODUCTION

Graphene, an allotrope of carbon which is consist of a single layer of carbon atoms that is arranged in a hexagonal lattice. It is the basic structural element of many other allotropes of carbon such as graphite, diamond, charcoal, fullerenes as well as carbon nanotubes. Due to the sp_2-hybridised orbital of the covalent bonds between the carbon atom in a graphene, it is widely known for its exemplary mechanical strength and causing it to be possible for a one atomic layer thick, stable free-standing graphene sheets to exist [1]. According to multiple studies that have been conducted [2], graphene also promises a large improvement in the electrical and electronic industries due to its high thermal conductivity [3].

With a tested mechanical strength of 1TPa, extraordinarily high thermal conductivity, as well as a large surface area of 2675 $m^2 g^{-1}$ [4], this characteristics of graphene have attracted many researcher to introduce graphene into many other application such as for conducting films, nanoelectronics as well as integrating with sensors in an electrical component [3]. Graphene sheets can be iterated into many other forms which is wrinkled, rippled and crumpled graphene (C-Gr). Due to the ball like structure of a C-Gr, it is identified to exhibit the high resistant to aggregation among the other form [4]. The C-Gr ball also indicates a much larger specific surface area as well as having a more

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open structure in comparison to the respective stacked flat sheets. Crumpling degree of a graphene can be visually determined by using a Transmission election microscopy (TEM) [5].

Over the years, there have been many other methods that is used to produce C-Gr [6]. There is the hydrothermal method, fast cooling method as well as mechanical method that is invented to produce high quality crumpled graphene [4]. This research however will focus more on the production of crumpled graphene using the fast cooling method [4]. The method of fast cooling is still under study and the effect of the method on graphene nanoflakes have not been fully studied yet. Previous study only focuses on fast cooling by using liquid nitrogen to flash freeze the graphene samples. This method of fast cooling is not a newly introduced method as studies have been conducted to determine the different method of crumpling graphene [4]. There are very few studies that have been conducted to investigate the effect of temperature lower than 0°C to graphene nanoflakes and studying the crumpling effect on the composition and degradation temperature of corrugated graphene. Temperature -20, -40 and -80°C is chosen based on the temperature availability of the freezer used which is currently operated at the given temperature.

METHODOLOGY

Crumpled Graphene Preparation

The formation of C-Gr begins by dispersing 0.5g of graphene powder into 200ml of distilled water. Three separate sample is prepared as the sample will be exposed to 3 different temperature of freezer at -20, -40, and -80°C. The mixture is then submerged into an ultrasonic water bath to ensure a more uniform dispersion of the graphene powder with frequency of 37 Hz at 100 percent power using the pulse setting for a duration of 30 minutes. Subsequently, each sample is stored inside three different freezers operating at temperature of -20, -40 and -80°C for a duration of 1 hour before all three sample is stored inside a chiller with a temperature of -20 to be left overnight for 24 hours. After the cooling process, the samples are taken out of the chiller and is left aside for 6 hours to be melted at room temperature. The centrifuge machine is used to separate the C-Gr from the melted distilled water. it is operated at 10000rpm for 30 minutes for each batch of samples. The heavier suspended C-Gr is collected at the bottom of the tube leaving the distilled water on the top section of the centrifuge tube waiting to be removed. The moisture content of the sample is then further removed through means of oven drying at a temperature of 60°C for 24 hours. The remaining solid collected at the bottom of the centrifuge tube is the desired C-Gr. However due to the apparatus limitation in this research, the crumpling degree of the graphene is determined by the diameter of the produced graphene, where a much smaller diameter of C-Gr represent a higher degree of crumpling as it undergoes a much efficient compression [7]. The degree of crumpling can also be determined using the Scanning Electron Microscope (SEM) to provide a visual representation for the crumpling of graphene nanoflakes. Table 1 show the concentration of sample A, B and C and the temperature which the sample will be freeze at.

TABLE 1. Crumpled graphene sample

Sample	Graphene, g	Distilled water, ml	Temperature, °C
A	0.05	200	-20
B	0.05	200	-40
C	0.05	200	-80

Sample Characterization

Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

A SEM is with an electron focused beam of electron is used with EDX to obtain visual representation of the surface topography with the sample composition. For SEM, each sample underwent 5 different measurement that is taken at

different resolution of 1,5,20,50 and 200µm. While for EDX each sample undergoes magnification of 10000 X with accelerating voltage of 20kV. The sample underwent 3 iteration for all element to be analyzed.

Thermogravimetric Analyzer

A thermogravimetric analyzer (TGA 8000, Perkin Elmer) is used to study the decomposition temperature of the C-Gr. The samples undergo TGA temperature analysis from 30 to 750°C with a ramping rate of 20°C in pure nitrogen gas.

Fourier-Transform Infrared Spectrometer

A single bounce diamond crystal Fourier-transform Infrared Spectrometer (FTIR, Perkin Elmer Spectrum 100) is used to study and analyze the functional group by detecting the chemical bond of each samples. The sample undergo scans at a resolution of 4cm^{-1} with a frequency ranging from 650 to 4000 cm^{-1}.

RESULTS AND DISCUSSION

Scanning Electron Microscope (SEM)

The results obtained from the SEM is shown for different temperature acted on the sample. Figure 1 shows the SEM images which is captured for sample A which is freeze at -20°C.

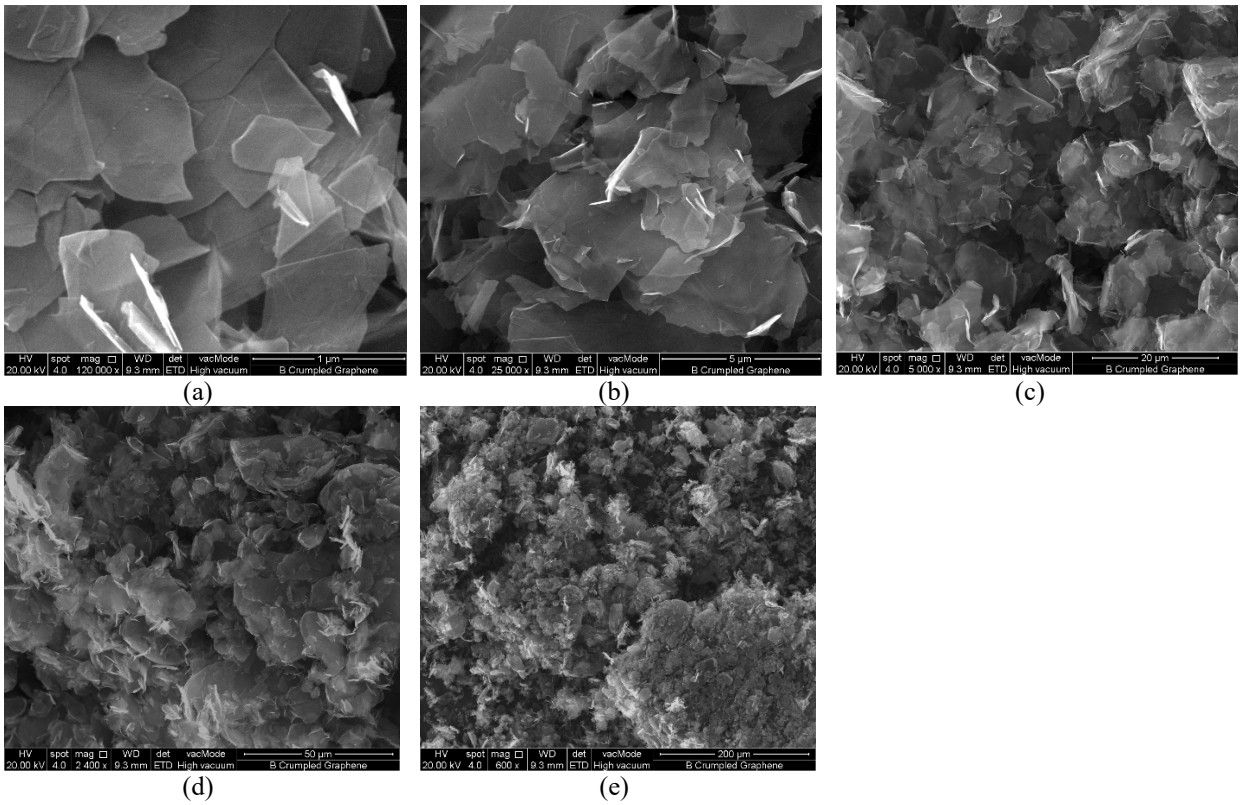

FIGURE 1. SEM images for sample A at (a) 1µm (b) 5µm (c) 20µm (d) 50µm and (e) 200 µm

Figure 1 (a) it shows little degree of crumpling occurring in the graphene nanoflakes. The temperature maintained at -20°C is not providing enough compression for the nanoflakes when it was subjected to the low temperature. Only

a few crumpling can be observed occurring at the edges of the nanoflakes. However, (c), (d) and (e), show quite significant amount of crumpling occur to the graphene nanoflakes. This still support the basis that crumpling still occur when subjected to temperature as low as -20°C.

Figure 2 shows the SEM images which is captured for sample B which is freeze at -40°C.

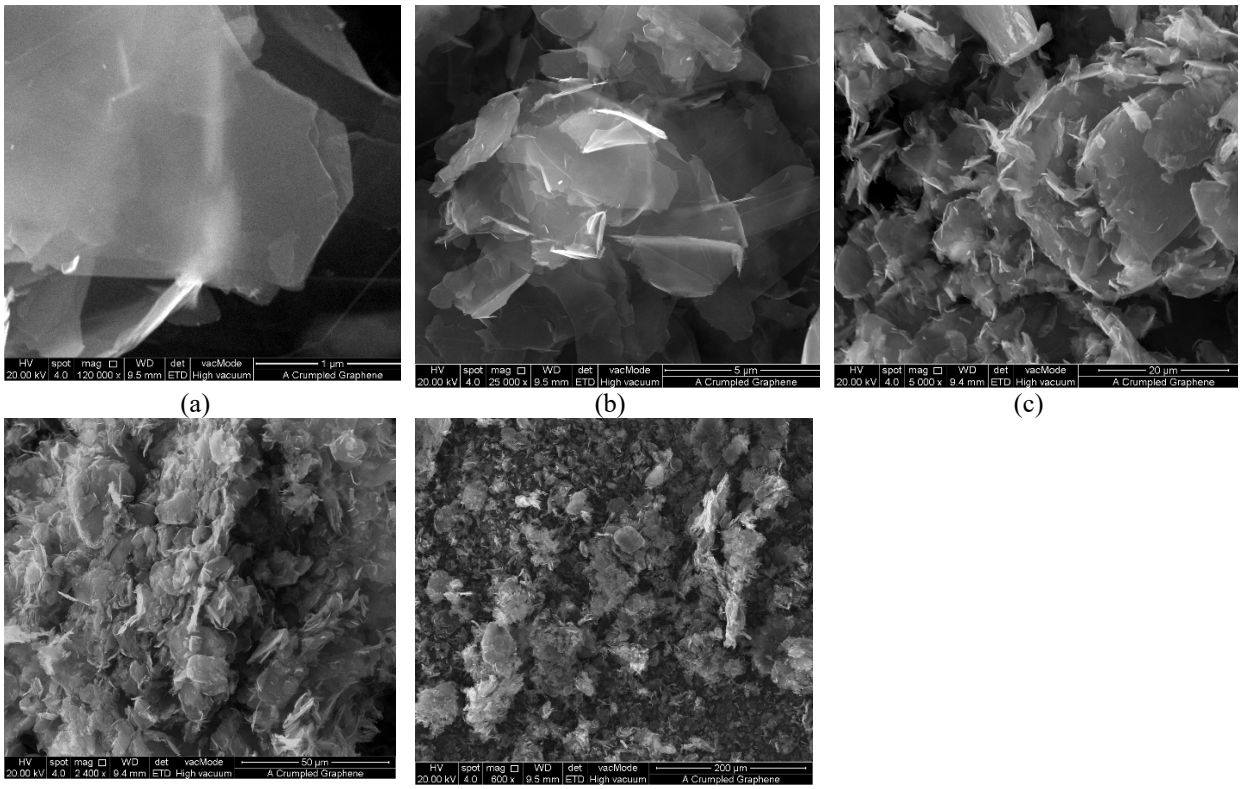

FIGURE 2. SEM results for sample composition B at (a) 1µm (b) 5µm (c) 20µm (d) 50µm and (e) 200 µm

Figure 2 (a) it shows a much high degree of crumpling occurring in the graphene nanoflakes compared to Figure 1. The temperature maintained at -40°C is providing quite a significant amount of compression for the nanoflakes when it was subjected to the low temperature. Crumpling can be observed occurring at the edges of the nanoflakes and formation of a ball like structure shown in Fig 3 (c). Fig 3 (d) and (e), shows significant amount of crumpling. This support the basis that crumpling occur when graphene nanoflakes is subjected to temperature as low as -40°C.

Figure 3 shows the SEM images which is captured for sample C which is freeze at -80°C.

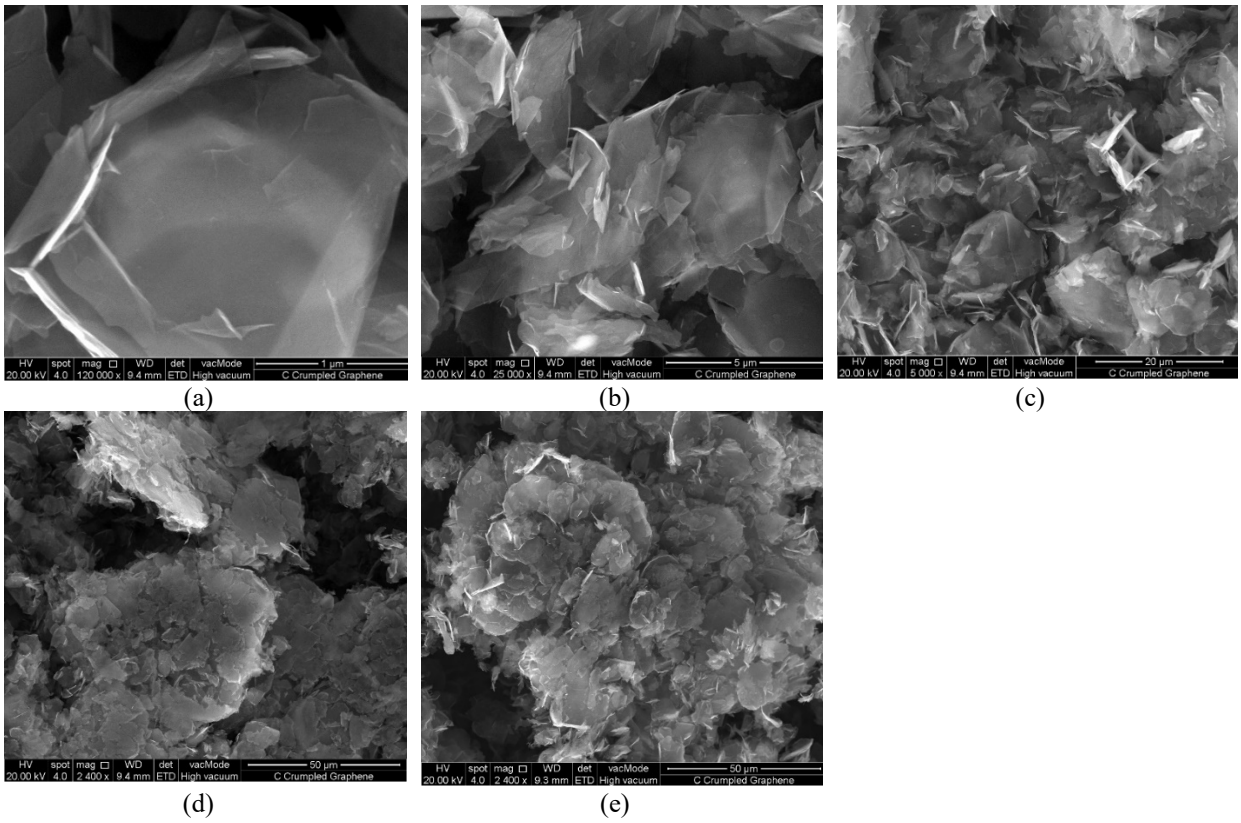

FIGURE 3. SEM results for sample composition C at (a) 1µm (b) 5µm (c) 20µm (d) 50µm and (e) 200 µm

Based on Figure 3, (a) it shows the highest degree of crumpling occurring in the graphene nanoflakes compared to Figure 1 and Figure 2. The temperature maintained at -80°C is providing a significant amount of compression for the nanoflakes when it was subjected to the very low temperature. The crumpling occurs in just 1-hour duration of storage. Crumpling can be observed occurring at the edges of the nanoflakes and formation of a ball like structure is occurring at (c). Images (d) and (e), shows significant amount of crumpling occur to the graphene nanoflakes. This support the basis that crumpling occur when subjected to temperature as low as -80°C. In comparison, the degree of crumpling is decided based on a single layer of graphene nanoflakes [4].

The difference is more noticeable when only the sample is tested on 1µm resolution. The lower the temperature the graphene nanoflakes is more clump together, this is due to the freezing condition of the mixture when exposed to low temperature. The dispersed graphene become more closely clump together when stored at lower temperature [8]. This continue to retain it shape until the drying process which causes the C-Gr to be less powdery. The moisture content of the sample may also a little higher and should be subjected to a much longer drying process in order to efficiently separate the C-Gr. All three samples a very distinct visual of being crumpled if compared to SEM image of a graphene [8].

The higher crumpling degree of graphene causes the diameter of the single graphene nanoflakes to decrease. At lower temperature, the colder temperature difference causes the graphene nanoflakes to crumple under a much rapid compression due to the solidifying of water molecule. As the nanoflakes is crumpled into a ball like structure, the outer layer of the nanoflakes is push inside due to the thermal contraction making the overall diameter of the graphene nanoflakes smaller. Thermal expansion and contraction can affect the assembly resistance of material. Through the generation of large stress, when at constant pressure, any decrease in temperature will cause a reduction of the physical dimension (diameter) of the body [9]. Causing the diameter or size of the graphene nanoflakes to decrease.

Energy Dispersive X-ray (EDX)

EDX analysis is commonly done simultaneously with SEM. The purpose of EDX analysis is mainly used for the elemental analysis or for the sample chemical characterization. For this sample however, the component is majorly graphene and oxygen as it there are no other chemical reaction subjected to the material for the synthesis of C-Gr. The purpose of this test is to ensure the graphene nanoflakes does not react with other chemical and to ensure there are no residue which can affect the crumpling of the graphene nanoflakes. The result shown are only one out of the three iteration taken.

TABLE 2. EDX results for sample A

Element	Weight (%)	Atomic (%)
Carbon	96.69	97.61
Oxygen	2.99	2.27
Sulfur	0.31	0.12

Table 2. show that the main component carbon is occupying the total weight of the component by 96.69 wt%. There is very small traces of other element such as oxygen and sulfur in the sample. This act as an evidence for the purity of the component as there are very little impurities in the sample and is acceptable to be used as experimental data.

TABLE 3. EDX results for sample B

Element	Weight (%)	Atomic (%)
Carbon	96.54	97.47
Oxygen	3.23	2.45
Sulfur	0.23	0.09

Table 3. show that the main component carbon is occupying the total weight of the component by 96.54 wt%. Although the value is a little less than the result in Figure 4, the amount of carbon occupying the sample is still very high. There is existence of other element such as oxygen with 3.23 wt% a little higher than in sample A and there is a small trace of sulfur in this sample. This act as an evidence for the purity of the component as there are very little impurities in the sample and is acceptable to be used as experimental data.

TABLE 4. EDX results for sample C

Element	Weight (%)	Atomic (%)
Carbon	94.45	95.90
Oxygen	5.22	3.98
Sulfur	0.32	0.12

Table 4. show that the main component carbon is occupying the total weight of the component by 94.45 wt%. The value is a little less than the result in Table 2 and 3, but the amount of carbon occupying the sample is still very high. There is existence of other element such as oxygen with 5.22 wt% a little higher than in sample A and traces of sulfur which is almost the same with sample A. The high amount of oxygen is probably caused by the inability for the drying process to completely remove the moisture due to the sample clumping together after subjected to the low -80°C temperature. The value obtained by this analysis act as an evidence for the purity of the component as there are very little impurities in the sample and is acceptable to be used as experimental data.

Thermogravimetric (TGA)

Thermogravimetric analysis is mainly used to measure the decomposition temperature of the samples. The decomposition temperature is important to determine the maximum operating temperature for the samples before it will decompose under extreme heat. The analysis is conducted at a starting temperature of 30°C to 900°C, ramping rate of 20°C with pure nitrogen. The result obtain from the characterization experiment is shown in Figure 4 below.

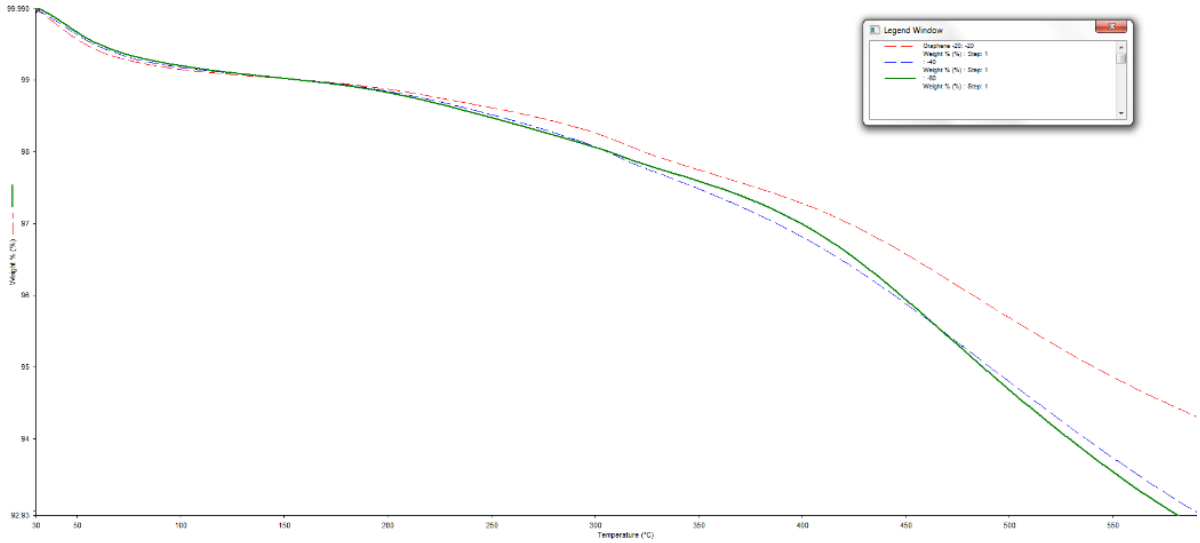

FIGURE 4. Combination result of sample A, B and C by weight percentage.

From Figure 4, sample A can be seen to decompose at a steady rate and continue to decompose until it stops at temperature ranging at 895.5°C. Sample B can be seen to decompose at a steady rate and continue to decompose until it stops at temperature ranging at 900.5°C and sample C can be seen to decompose at a steady rate and continue to decompose until it stops at temperature ranging at 897.5°C.

Figure 4 compare the results obtain from the TGA analysis of all the sample. It can be seen that sample A at -20 °C have the less weight loss at the 550 °C temperature and sample C is the first one to decompose completely first at a temperature at 580°C. The rate of decomposition can be seen to exponentiate quickly after the 400°C mark. Before reaching that temperature, the weight loss is still low for all three sample which indicate that the crumpled graphene can safely operate till 450°C, any temperature higher than that may cause the sample to decompose at a faster rate

Fourier-Transform Infrared Spectrometer (FTIR)

The FTIR is conducted on all samples of A, B and C. The result of FTIR is shown in Figure 5 below.

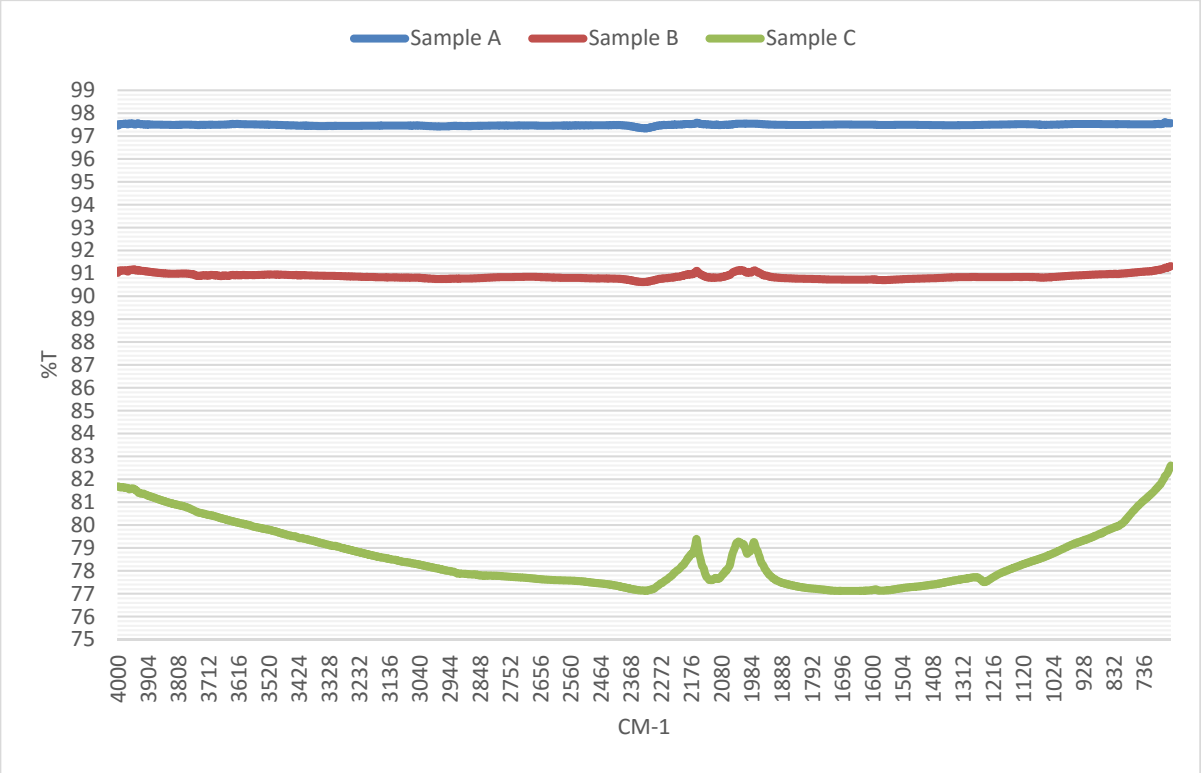

FIGURE 5. Combination of FTIR results for sample A, B, and C.

From Figure 5, it can be seen that there the are a few spike on the sample A spectra value. It can be seen that the graph peak at around 3000~, 2400~ and 1400~ cm^{-1}. These are among the most visible spike on the sample spectra. There are some other peak can be noticed in the spectrum however due to the sheer amount of peak existed in the Figure, only the most visible peak is taken into consideration for discussion. At 3000~ cm^{-1} this range the peak is mainly due to the presence of the C-H stretching. The 2400~ cm^{-1} indicated the symmetrical stretch of the $C-O_2$ group as well. And for 1400~ cm^{-1} indicate the presence of the C-O group existing in the sample.

The spectrum peak for sample B can be notices to exist at the 3000~, 2400~, 2000~, 1500~ and 1000~ cm^{-1}. There are more noticeable peaks at the sample B which is probably due to more compression is applied to the sample at a lower temperature. We can see that the transmittance value also decreases for sample B. For the value 3000~ cm^{-1} this is due to the presence of C-H functional group in the sample. Next peak at a value 2400~ cm^{-1} which indicated the presence of the $C-O_2$ group. For 2000~ cm^{-1} the functional group which can be determined is the C=O. At 1500~, and 1000~ the group C=C and C-O is the one responding to the transmittance [10] .

Sample C have a different curve of peak compared to the other sample presented before this. The peak is a lot more noticeable and much lower transmittance can be detected. The peak can be found at the 3000~, 2300~, 2000~, 1700~,1500~, 1300~ cm^{-1}. Each peak indicates the existence of difference functional group. Similar to Figure sample B, 3000~,2400~, 1500~ and 1300~ cm^{-1} indicate the presence of C-H, $C-O_2$, C=C and C-O respectively. The wavelength of 1700~ indicating the presence of C=O group.

For all three samples, the most visible peak is located at the 1500 – 2400 cm^{-1} peak range. The peak at this wavelength shows the presence of the excitation of the π electron exist in graphite structure [10]. Which indidcates the existance of the C-C and C-O bond that should be presence in all three samples.

CONCLUSION

The aim for this study is to investigate the effect of low temperature on the structural morphology of a graphene nanoflakes. When subjected to different temperature below 0°C, the graphene nanoflakes is applied with high compression due to the solidification of the water molecule in the mixture. As the temperature acted on the graphene become lower, how does the structure of the graphene morph to follow this temperature change. The sample is also tested by using SEM to study the surface morphology of the graphene nanoflakes, it can be seen that at a lower temperature of -80°C, a much higher crumpling degree will occur. Due to the higher compression and rate of solidification of water molecule in the mixture, the nanoflakes is squish in between a solidifying water molecule for a much longer time. Next test is the EDX which is done to determine the chemical composition ensuring there are no impurities presence in the sample as it will be able to affect the diameter of the graphene crumpling. For the TGA test, the decomposition temperature for each sample can be stated to be equal to each other as the result does not show a very significant difference in the rate of decomposition for different samples and crumpling degree. And finally, the FTIR analysis which is to determine the existence of certain functional group and bonding in the samples. All three samples excite the wavelength where the functional group of C-C and C-O exist indicating the major presence of these component. Thus, it can be concluded that when using the fast cooling method at -80°C, high quality crumpled graphene can be produced and be repurpose into other applications.

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