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ANALYSIS OF CRUSHED MULTI-WALLED CARBON NANOTUBES

Rike Yudianti, Ferensa Oemry, Lucia Indrarti, and Holia Onggo
Research Center for Physics, Indonesian Institute of Sciences
Jalan Cisitu No. 21/154 D Bandung

ABSTRACT

ANALYSIS OF CRUSHED MULTI-WALLED CARBON NANOTUBES. Crushing Multi-Walled Carbon Nanotubes (MWCNTs) by cryogenic crusher is one of mechanical methods to create good dispersion Carbon Nanotube (CNT) as structural modification of MWCNT for potential hybrids materials. Crushing in 15 and 30 minutes effectively cut tubes to be shorter and densely-packed structure formed after crushing 30 minutes. Based on Raman spectroscopy and thermal behavior of crushed MWCNTs, functionalization of MWCNT unidentified after crushing. Burn temperature of crushed MWCNTs (601.6 ^oC and 603.6 ^oC) appeared to be sooner than that's of pristine MWCNT (642.2 ^oC). The low oxidation resistance of crushed MWCNT pointed out presence of defective carbon corresponding to too short-CNT due to cutting.

Key words : MWCNT, Crushing, Carbon Nonotube, Short-CNT

ABSTRAK

ANALISIS HANCURAN KARBON *MULTI-WALLED NANOTUBES*. Penghancuran *(Crushing)* dengan *cryogenic crusher* merupakan salah satu metode mekanik untuk menghasilkan dispersi karbon *nanotube* (*CNT*) yang baik sebagai modifikasi struktural karbon *multi-walled nanotube* (*MWCNT*) untuk material hibrida yang potensial. *Crushing* selama 15 menit dan 30 menit efektif memperpendek *tube* dan struktur rapat terbentuk setelah *crushing* 30 menit. Hasil Raman spektroskopi dan analisis termografimetri hancuran *MWCNT* menunjukkan bahwa setelah *crushing* tidak terbentuk gugus fungsi. Suhu oksidasi hancuran *MWCNT* (601,6 ^oC dan 603,6 ^oC) lebih cepat dari pada *MWCNT* murni (642,2 ^oC). Ketahanan oksidasi yang rendah dari hancuran *MWCNT* menunjukkan adanya *CNT* yang sangat pendek dari karbon yang rusak akibat *crushing*.

Kata kunci : *MWCNT, Crushing, Carbon nanotube, CNT* pendek

INTRODUCTION

Carbon nanotubes (CNTs) are one of the most interesting nanomaterials because of their excellent characteristics of their remarkable strengths [1,2] elasticities [3,4] and super electrical properties [5].Their properties are potential use for several applications such as the reinforced materials in CNTs-polymer composite [6-8]. To speed up the CNTs applications, the problem of removing the impurities should be addressed first to have free CNTs from carbonaceous and non-carbonaceous compounds should remain embodied in the material geometry.

Many approaches were employed to functionalize single-walled nanotubes (SWNTs) with functional groups non-covalently [9] or covalently [10-12] to create highly stable dispersions. Therefore, strategic approaches toward the solubilization of CNTs are essential for their applications. Much effort has been made to develop approaches for reproducible dispersion of individual carbon nanotubes. Mechanical dispersion methods, such as ball milling and high shear mixing disperse nanotubes from each other, can also decrease fragment the nanotubes.

Functionalization is often conducted by treatment of the nanotubes in appropriate chemical oxidation under ultra-sonication or reflux conditions using a mixture of strong acids [13-16] or exposing them to vapors at high temperatures [17] as a generally known method to cut CNTs. However, the acid treatment has several disadvantages such as loss of materials [18] causing some methods are being developed to create short-CNTs by ball milling [19-22].

In this study, preparation of short-CNTs was performed by cryogenic crusher as one of mechanical treatments to result in good dispersion CNTs. This study is intended to know effectiveness of cutting tube in rigid condition by cryogenic crusher. Quality of crushed multi-walled carbon nanotube (MWCNT) was analyzed by Raman Spectroscopy, Termogravimetri and Scanning Electron Microscope (SEM). Raman spectroscopy was used to ansure absence of functionalized MWCNTs

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formed by cryogenic crusher. Morphological properties of shorter CNTs produced by cutting were clearly observed by SEM.

EXPERIMENTAL METHOD

Multi-walled Carbon Nanotubes (MWCNTs) purchased from Chengdu Alpha Nano Tech. Co. Ltd. were used without further purification. Weight of 50 mg MWCNT was placed in 50 mL crushing cell which is attached to the crushed rod and rod attached to the main unit. The crushing cell was immersed in liquid nitrogen poured to the vessel to maintain samples at low temperature during crushing. After pre-cooled for 5 minutes, crushing was performed by Cryogenic Crusher, JFC 300, controlled for 15 (crushed MWCNT-15) and 30 minutes (crushed MWCNT-30). After crushing, cell was placed in the flowing water to elevate the cell temperature and subsequently dried in 45 °C.

Crushed MWCNTs were evaluated by Raman Spectroscopy, TGA and Scanning Electron Microscope (SEM). Raman spectra were recorded on 1000 micro-Raman system, with a charge-couple device detector. A He-Ne laser with excitation energy of 1.96 eV served as excitation source, with a spot size of ±1 mm in diameter. The morphological surface of MWCNT was observed by Scanning Electron Microscope (SEM), JEOL JSM-6360LA at 20 kV after dispersion of 0.5 mg MWCNT in 50 mL ethanol by ultrasonic vibration. Dispersed MWCNT was dropped on the surface of SEM sample holder and allowed to dry in air. Thermogravimetric analysis (TGA) was performed by Setaram SETSYS-1750. The measurement was conducted by heating of 9-12 mg samples in platinum pan with 5 mm diameter, in dry air from 35 up to 1000 °C at rate of 10 °C/minute.

RESULTS AND DISCUSSION

Analysis of short MWCNTs was successively conducted using thermogravimetri, Raman Spectroscopy and SEM, as common characterization techniques. Crushed MWCNTs were compared with pristine MWCNT to know effectiveness of cutting with respect to crushing time to create shorter tube without damaging side walls. The Raman spectra should be distinguished from other carbonaceous materials by the presence of two distinct feature, D-band at 1,300 cm^{-1} and the G-band between 1,530-1,610 cm^{-1}.

Raman spectroscopy as powerful technique was used in this study to analyze functionalization of CNTs. Figure 1 showed that crushed MWCNT-15 and MWCNT-30 did not form D-band at 1,300 cm^{-1} corresponding to a double resonance process and diorder sp^2 carbon defect in graphitic sheet [23] and amorphous carbon present as impurities [24]. The absence of D-band revealed that functionalization of

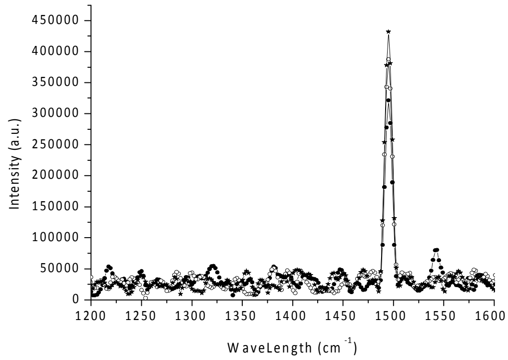

Figure 1. Raman Spectra of MWCNTs : (a) Pristine MWCNT, (b) Crushed MWCNT-15, (c) Crushed MWCNT-30; (□ Pristine MWCNT ; ○ Crushed MWCNT-15; ● Crushed MWCNT-30)

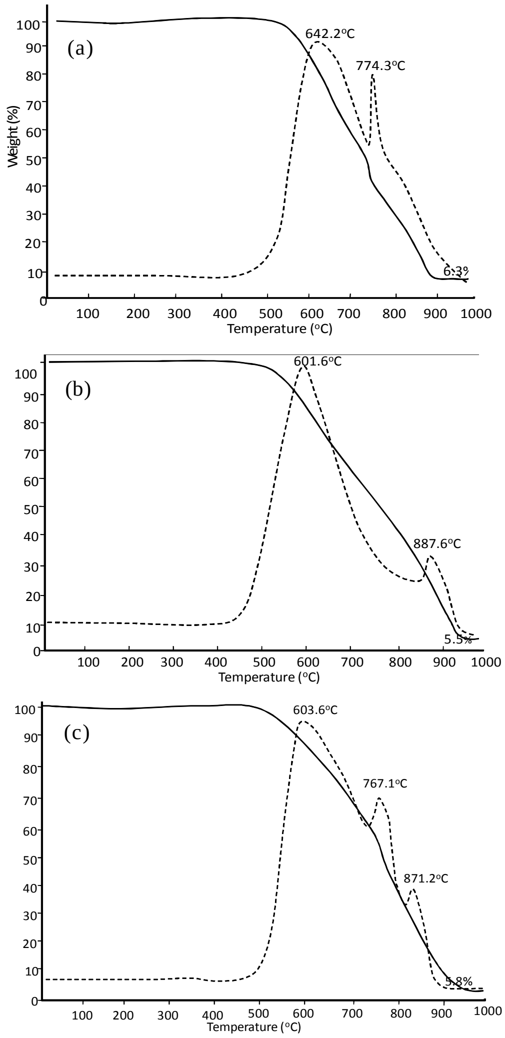

Figure 2. TG/DTA profiles of MWCNTs : (a) Pristine MWCNT, (b) Crushed MWCNT-15, (c) Crushed MWCNT-30

CNTs did not occur after crushing. Crushing caused the intensity of G-band at 1,530-1,610 cm^{-1} reduced by increasing crushing time. The reducing elucidated a destruction in characteristic of sp^2 carbons on the hexagonal graphene network. This condition was supposed as unstable carbon originated from too short carbon.

Since TGA/DTA as widely used method to determine the level of purification, analysis of the thermal behavior of purified MWCNTs was conducted by TGA. Quality of crushed MWCNTs was also confirmed by thermogravimetri analysis (Figure 2) in air to study oxidative response by comparation performance of crushed MWCNTs and pristine MWCNT. The MWCNTs were evaluated based on the extent of oxidizable compounds from carbonaceous impurities. The solid and the dot lines corresponded to TGA and DTA, respectively.

TGA curve of pristine MWCNT shows absence of oxidizable compounds at low temperature (300-500 ^{o}C), considered as free carbonaceous MWCNT. After saturation, two stepwise weight loss peaks at 642.2 and 774.3^{o}C attributed to oxidation of MWCNT and graphitic components, respectively remaining 6.3% as non-oxidizable residues as metal oxide or metal-related components. Low oxidation resistance was evidently observed in crushed MWCNTs. Thermal behavior of crushed MWCNT-15 (Figure 2b) shows two peaks in DTA trace, oxidation peak of crushes MWCNT at 601.6 ^{o}C and oxidizable compounds at 887.6^{o}C, supposed as contaminant materials origin from crushing cell during process. Presence of impurities and shorter CNTs affected quality of MWCNTs by reducing burned temperature of MWCNTs to be lower (601.6 ^{o}C). Crushed MWCNT-15 still contained non-oxidizable residues as mixtures of metal oxides or metal components, approximately 5.5%. In crushed MWCNT-30, three stepwise oxidation occurred corresponding to oxidation peak of CNTs at 603.6 ^{o}C, graphitic nanoparticle at 767.1 ^{o}C and contaminant materials at 871.2 ^{o}C. Low oxidation temperature of carbon pointed out presence of amount of unstable carbon from short-CNT. Crushing 30 minutes ineffectively removed graphitic particles and remained non-oxidizable compounds, estimated about 5.8%.

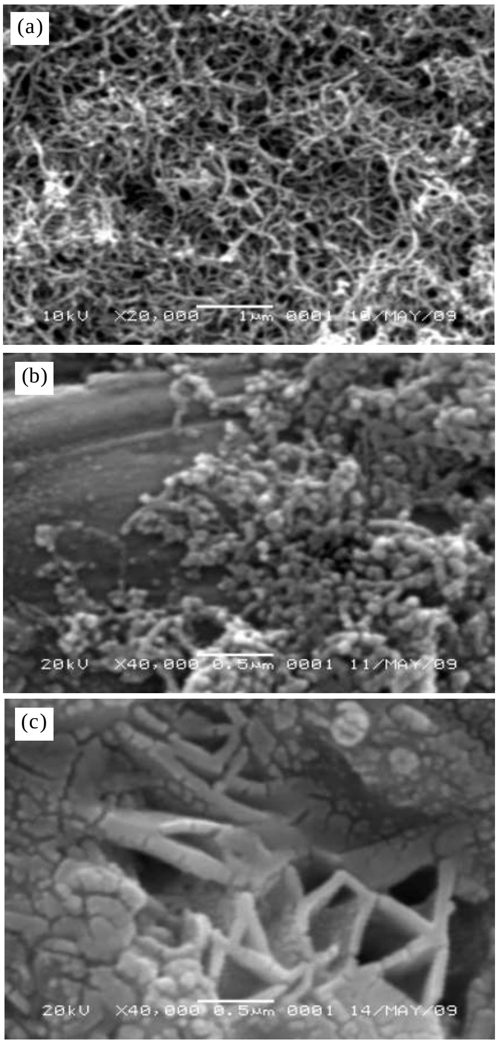

Figure 3. Morphological Properties of MWCNTs : (a) Pristine MWCNT, (b) Crushed MWCNT-15, (c) Crushed MWCNT-30

On the results of morphological properties, the pristine MWCNT showed folded and bundles of fibers (Figure 3a). Adherence of amount of particle-like impurities was clearly observed in the figure. Cotton-like entanglements seem to form agglomeration inhibiting separation in some location and infiltration with the matrix. Crushing for 15 and 30 minutes produced shorter CNTs and consequently enhanced existence of agglomeration of tubes. It is understandable that shorter CNTs did not simultaneously followed by formation of functional groups in which formation of functional groups made good dispersion of individual threads. Agglomerate CNTs tend to form in the shorter CNTs of crushed MWCNT-15. Densely-packed structure was clearly observed in Figure 3c, whereas crushing might cause losses amount of CNTs to be unstably too short MWCNTs as multi-layered polyaromatic carbon content of the sample.

The multi layered polyaromatic carbon material originates from the collapsing of MWCNTs into graphene planes. Significant destruction of side walled of CNT also occurred in the long ball milling times as elucidated by Pierad *et.al*. [25]. Crushed MWCNT-30 have a densely-packed structure in which the individual MWCNTs are fractured and flattened with increase in the crushing time.

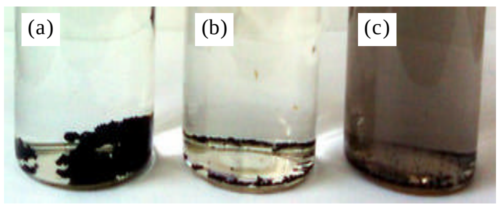

Figure 4. Photograph of dispersibility behavior of (a) pristine MWCNT ; (b) Crushed MWCNT-15 ; (c) Crushed MWCNT-30, after 20 days. Content of MWCNTs in each bottles is 0.1 mg/mL, ultrasonicated for 2 hours without addition of surfactan

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Quality of purified MWCNTs was given through dispersibility test in water without addition of surfactan (Figure 4). Pristine MWCNT formed clear-cut separation with water even in crushed MWCNT-15, eventhough some amount of dispersable CNTs was observed. Presence of impurities attached to the tubes and Van der Waals attraction between tubes caused hydropobicity of tubes in making low dispersibility in water. Dispersibility of MWCNTs was found to significantly enhanced after crushing for 30 minutes eventhough unstable carbon formed during process. Presence of unstable carbon was analyzed by Raman Spectroscopy and confirmed in morphological structure of CNTs as serious damage in side wall. However in the processing for 30 minutes, the shortest CNT was produced in making more dispersable CNT (Figure 4c). It revealed that crushing method for the production of short-CNTs is believed to be fundamental techniques to convert long, entangles CNT into more dispersable.

CONCLUSIONS

Short MWCNTs produced by cryogenic crusher significantly enhanched their dispersibility after crushed for 30 minute in despite of destruction of MWCNTs arised after crushing. Crushing for 30 minutes, an partial disruption of the tubular structure and the formation of multi-layered polyaromatic material supposedly occurred, observed in densely-packed structure in the morphological surface. Otherwise, its dispersibility ineffectively improved in the lower crushing time (15 minutes).

In the future, the optimum time of treatment to cut MWCNTs, to keep the tubular structure and to maximise their specific surface will be considered in addition to ball materials that can also modulate the products should be done.

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