Characterizations of carbon nanotubes grown on clay

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Abstract. Carbon nanotubes (CNTs) are nano materials that have unique physical and mechanical properties. Carbon nanotubes grown on clay (Clay-CNTs) are new hybrid material based on clay mineral. Clay minerals were used as catalyst for CNTs synthesis by chemical vapor deposition at 700 °C for 1 hour. In this work, Clay-CNTs were investigated by various analytical techniques such as X-ray diffraction (XRD), scanning electron microscope (SEM) and electron diffraction spectrometer (EDS) and Raman spectroscopy to analyse the phase identification of crystalline, morphology and crystallinity quality of Clay-CNTs. Moreover, thermogravimetric analysis (TG) was studied to identify phase decomposition. XRD results indicate crystallites of the CNTs have (002), (101) and kaolinite and quartz from clay mineral catalyst. SEM images of Clay-CNTs showed cluster of CNTs on carbon fiber and their worm-like morphology. The intensity of Raman spectra of Clay-CNTs reveals the defect of CNTs structure. TGA derivative profile indicated decomposition of CNTs and kaolin.

1. Introduction
Carbon nanotubes (CNTs) are made up hexagonal of carbon atoms in the cylinder shape with radius in nanometers [1]. Chemical vapor deposition (CVD) is mostly used for synthesis of carbon nanomaterials [2] due to its low cost and scalable method for mass production compared to other methods [3]. The different hydrocarbon (acetylene, ethylene, ethane and methane) were used as carbon sources [4]. Among the mostly used metal catalyst are Fe, Co and Ni due to high carbon diffusion rate is these metals and the high solubility of carbon in these metals at high temperature. CNTs can grow on support material directly such as silicon or metal substrates. However, catalyst materials are difficult to diffuse into substrate [5]. Clay minerals were used as replacement catalyst supported materials such as kaolin [6] and montmorillonite [7]. The advantages of used clay as supported catalyst are low cost [8] and ion-exchange [4]. Moreover, clay also contains several oxides such as Fe₂O₃, SiO₂, Al₂O₃, CaO, TiO₂, MgO and others. The literature reported that the growth of CNTs on clay mineral were prepared by wet impregnation with using Fe(NO₃)₃ as catalyst for Fe intercalated on clay mineral [6]. In this work, the production of Clay-CNTs was growth directly on clay mineral by...
chemical vapor deposition. The process of Clay-CNTs was synthesized according to Warakulwit et al [2]. CNTs grown on clay (Clay-CNTs) were characterized by quantitative analysis and to identify the phase structure by X-ray diffraction. In addition, morphology of Clay-CNTs was investigated by scanning electron microscope and the phases were characterized by thermal analysis.

2. Characterization methods
CNTs grown on clay (Clay-CNTs) were supplied by Siam Research and Innovation Co., Ltd. Clay-CNTs were grown by chemical vapor deposition at 700 °C for 1 hour. The quantitative phase analysis of raw clay was analyzed by X-ray powder diffraction (XRPD) with Bruker AXS (D4 ENDEAVOR). X-ray diffraction was investigated in the 2Θ range from 10° to 60°, in steps of 0.01° and speed is 10 degree per minute by Rigaku SmartLab diffractometer (CuKα at room temperature). Clay-CNTs were dispersed by sonication before observing the morphology by Scanning electron microscope (SEM; JSM -IT300) and the elements of Clay-CNTs were determined by energy dispersive spectroscopy (EDS). The crystalline quality of Clay-CNTs was evaluated by Raman spectrometer with a 514.5 nm argon ion laser (Jobin Yvon Horiba T64000). Moreover, Clay-CNTs mass were determined by thermogravimetric analyzer (TGA8000; Perkin Elmer) at room temperature to 1,000 °C using a heating rate of 10 °C/min in nitrogen atmosphere.

3. Results and discussion
3.1. XRD
The quantitative phase composition of raw clay used for catalyst is shown in table 1. The main phases of raw clay include kaolinite phase (30.88%) and amorphous phase (38.70%). Furthermore, hematite (Fe₂O₃) is found at 2.98% to be catalyst for growth of CNTs. The X-ray diffraction (XRD) pattern of Clay-CNTs is shown in figure 1. The XRD results indicated the peaks of carbon phase and clay mineral catalyst. The peaks at 2Θ = 26.2° and 44.3° correspond to (002) and (101) respectively that is the reflection of carbon phase. Moreover, XRD pattern shows that the clay mineral is composed of kaolinite, quartz and calcite. The sharp peaks of XRD patterns at 2Θ values of 20.8°, 26.6°, 36.5°, 39.4° and 50.1° represent crystalline of quartz. The XRD peaks of kaolinite are found at 19.9°, 25.3°, 36.0° and 46.0°. Furthermore, few diffraction peaks indicating calcite was found. The cementite is also found in figure 1 which is the main iron product. The cementite (Fe₃C) formation converted from the iron [9] which contains in clay mineral in chemical vapor deposition process. Furthermore, XRD pattern also shows an amorphous metakaolin which related to phase transformation from kaolin clay mineral [10].

Table 1. Quantitative analysis of raw clay (%).

| Kaolinite | Quartz | Hematite | Goethite | Anatase | Magnesiochloritoid | Gibbsite | Amorphous | Total |
|-----------|--------|----------|----------|---------|-------------------|----------|-----------|-------|
| 30.88     | 4.51   | 2.98     | 5.62     | 2.38    | 9.14              | 5.79     | 38.7      | 100   |

Figure 1. XRD pattern of Clay-CNTs.
3.2. Morphology

Morphology and quantitative elements analysis of Clay-CNTs are presented in figure 2. It can be seen that the cluster of CNTs deposited on the surface of carbon fiber in figure 2(a) and figure 2(b). Moreover, CNTs were rooted on clay particle that linking like network structure in figure 2(c) and also formation coverage on clay mineral surface as non-uniform and entangled as can be seen in figure 2(d). The structures of Clay-CNTs are worm-like morphology and show poor dispersion on clay mineral catalyst. The elements of Clay-CNTs found are C, O, Al, Si and Fe in different proportion. C obtained from CNTs and carbon fiber while the elements of Si, Al, O and Fe are originated from clay mineral catalyst.

![Figure 2](image_url)

**Figure 2.** SEM images with different magnification (a) 600× (b) 2,000× (c) 10,000× (d) EDS of Clay - CNTs.

3.3. Raman spectra

Figure 3 shows Raman spectra obtained for the Clay–CNT. The spectrum shows two strong peaks in the Raman-range 800 - 2220 cm⁻¹. D band and G band of Clay-CNTs appear at 1337 cm⁻¹ and 1574 cm⁻¹, respectively. The D-band corresponds to disordered carbon defects of the CNTs and impurities. While the G-band corresponds to stretching of C=C. To measure the crystallinity of Clay-CNT, the ratio of intensity of D band and G band (I_D/I_G) were calculated that relate to the degree of disorder in the graphite. The Value of I_D/I_G is 1.32 the same as literature report I_D/I_G = 0.52 - 1.88 [11]. However, the high intensity of D band than G band represents the defect of the graphite structural that may occur due to the defects of lattice such as pentagons, heptagons and vacancies [12-13].

3.4. Thermogravimetry analysis (TGA)

The weight loss and the first derivative of weight loss profile of Clay-CNTs are shown in figure 4. The initial weight loss decomposed at 30 °C continues until 200 °C was attributed to the physiosorbed and chemisorbed water molecules [6]. The degradation temperature range of 400 °C - 780 °C corresponds to kaolinite phase related to CNTs. The next degradation temperature of 780 °C - 920 °C may be attributed to calcite (CaCO₃) and carbon (CNTs) 920 °C - 1,000 °C which is the product from Clay-CNTs synthesis. The decomposition of CNTs agreed with that reported by Chaipanich et al [14].
4. Conclusions
Clay-CNTs, the hybrid material showed the morphology of Clay-CNTs cluster covered on the clay surface. The XRD pattern shows diffraction lines both of CNTs and clay mineral such as kaolinite and quartz. Furthermore, calcite and cementite, these are products from Clay-CNTs synthesis, also appear in XRD results. The SEM images showed the tubes of Clay-CNTs have worm-like morphology and network of Clay-CNTs between clay particles. Raman spectra appear D band higher than G band which corresponds to the defect in CNTs structure. Decomposition of kaolinite phase was found in TGA and DTG curves. Moreover, calcite and carbon phases were also found in Clay-CNTs.

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