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Carbon nanotubes formation on clay and fly ash from catalytic thermal decomposition of recycled polypropylene

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Abstract. Fly ash, plastic waste, and clay are mineral materials and residues commonly found in Malaysia. In this study, these materials were fully utilized as raw materials for synthesizing carbon nanotubes (CNTs). Recycled polypropylene, previously used as a food container, served as a carbon source. Fly ash and clay were explored as potential substrates for CNTs growth. The recycled polypropylene was thermally decomposed at 900 °C in an inert environment for 90 minutes. Carbon atoms released during this process were deposited on fly ash and clay substrates, which had been immersed in a ferrocene solution to provide a metal catalyst for CNTs growth. The deposited products were characterized using a Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD). Morphological analysis revealed that both fly ash and clay were coated with fiber-like structures, confirmed to be CNTs based on a diffraction peak around 26° from the XRD pattern. In conclusion, clay and fly ash demonstrate the potential to be utilized as substrates for CNTs formation.

Keywords: catalytic thermal decomposition; clay; CNTs; fly ash; recycled polypropylene

1. Introduction

Carbon nanotubes (CNTs) are nanoparticles with cylindrical tubular forms that are nanometers in size. CNTs are formed by rolling graphene sheets and are classed as single-walled or multi-walled depending on the number of layers of graphene sheets utilised (Helmannova *et al.* 2022) The diameters range of graphene from less than one nanometer to tens of nanometers, depending on how these graphene layers are wrapped into a cylinder (Venkataraman *et al.* 2019). Depending on the number of layers, carbon nanotubes can be single-walled (SWCNTs) or multi-walled (MWCNTs). CNTs are nano-architectured allotropes of carbon with wrapping graphene sheets producing a cylindrical shape. The diameter of most SWCNTs ranges from 0.4 to >3 nm, whereas the length can

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reach a few million times the diameter. SWCNTs are formed by folding a layer of graphene into the shape of a tube, whereas MWNTs are formed by multi-wrapped layers (concentric tubes) of graphene. The interlayer spacing in MWCNTs is about identical to the space between graphene sheets in graphite, which is 3.4 Å. MWCNTs have diameters ranging from 1.4 to at least 100 nm. CNTs are a type of carbon allotrope with unique features that make them valuable materials for us in nanotechnologies such as electronics, optics, and medicines. They have distinct qualities such as strength and strong electrical and heat conductivity (Liani *et al.* 2022).

Chemical vapour deposition (CVD) is the most effective technology for large-scale CNTs control in recent years, because of its simple equipment, ease of operation, and cheaper cost (Xiao-Di *et al.* 2019). When compared to other technologies, CVD is a low-cost, high-productivity, scalability, easy controllability, and possibly adaptable technology for future power and electrical devices (Saputri *et al.* 2020). CVD is a common growth technique because it can produce CNTs at low temperatures and with greater control over growth parameters, as well as develop CNTs on specific parts of a substrate (Ahmad and Silva 2020). The quality of the substrates used in the creation of carbon nanotube forests is particularly important, as the capacity of the catalyst to adhere to the substrate surface may have a substantial influence on the end product's properties. Using various substrates to gain information about the structure of carbon nanotube forests and the incorporation of nitrogen into their structures is a key step. Furthermore, the characteristics of the substrates can have a major impact on the structure and height of carbon nanotube forests (Szabó *et al.* 2020).

The environment around us is totally affected by the thrown plastic. For example, increasing in landfill, and a die out of birds and marine species. Thus, the concept of plastic recycling is actively spreading and practiced around the world. Converting plastic waste into valuable products such as carbon nanomaterial is important and is considered an option for industries and for environmental protection. In CVD process, the synthesis of CNTs involves many parameters such as carbon precursor and reactor temperature. Polypropylene (PP) is a polymer that incorporates a high carbon yield (85.71%) which makes it suitable to act as a carbon precursor in CVD (Sim 2017).

Fly ash is a fine-grained loose substance that is created as a byproduct of coal combustion. Toxic heavy metals found in fly ash include Hg, Cr, Ni, Pb, V, As, and Se. When the concentrations of such hazardous heavy metals exceed their usual values, it can have serious impacts on human and animal health (Ramanathan *et al.* 2020). Reusing fly ash has the potential to minimise disposal volumes and costs while also replacing non-renewable or expensive resources (Bhatt *et al.* 2019).

Clays and clay minerals are naturally occurring minerals that are inexpensive, non-toxic and have been employed as adsorbents in the treatment of water. Clays that have been modified with heat, surfactants, acids, or organic-inorganic modification have a limited adsorption capacity and re-generation ability for organic water contaminants (Ewis *et al.* 2022) The most complex process tailing to dewatering is waste clay slurry. This issue is linked to three key factors: highly tiny particle size, significant clay concentration, and system electrochemistry (Eskanlou and Huang 2021). In the CVD process, synthesis starts with the synthesis of carbon nanotubes (CNTs) which involves clay and fly ash as substrates. Substrates serve as foundational material where CNTs can grow (Shah and Tali 2016). Utilizing these substrates can significantly reduce the cost associated with purchasing expensive materials, which are typically high-priced. This development is intriguing and is currently being explored as a viable option for both industry and environmental conservation.

The main objective of this research is to study the feasibility of clay and fly ash to be used as substrate in CNTs growth from the thermal decomposition of recycled PP using the CVD method. By analyzing the crystal structures of both substrates before and after CVD, valuable insights can be gained into understanding on the CNTs formation that can be tailored for composite applications

in the future.

2. Materials

Recycled polypropylene (PP)-based plastic food containers served as carbon precursors for the CVD process. Clay and fly ash acted as metal catalyst substrates. Ferrocene (98%, Sigma-Aldrich), acetone (99.5%, Sigma-Aldrich), and argon gas were commercially purchased. Acetone was used to dissolve ferrocene, which was performed as a metal catalyst. Clay was obtained from a Perlis pottery manufacturer, and fly ash was industrially derived from coal combustion. Both functioned as substrates for metal catalysts used.

3. Methodology

3.1 Carbon precursor and substrate preparation

The plastic food container was washed, air-dried, and scissor-shredded into small pieces. 0.8 g of fly ash was added to the mixture of 0.6 g of ferrocene in 200 ml of acetone. The suspension was magnetically stirred for 3 hours followed by filtration. The residue was then dried at 100 °C for 10 minutes. The same procedure was repeated with clay.

3.2 CVD method

1.50 g of recycled PP and 0.20 g of ferrocene-treated substrates (clay or fly ash) were placed inside the CVD reactor as the arrangement shown in Fig. 1. First, the furnace was heated to 400 °C and maintained at this temperature for 10 minutes to thermally-decomposed the recycled PP. Then, the furnace temperature was raised to 900 °C and held for 90 minutes to deposit the decomposed carbon onto the treated substrate and grow the CNTs. After that, the furnace was cooled for 90

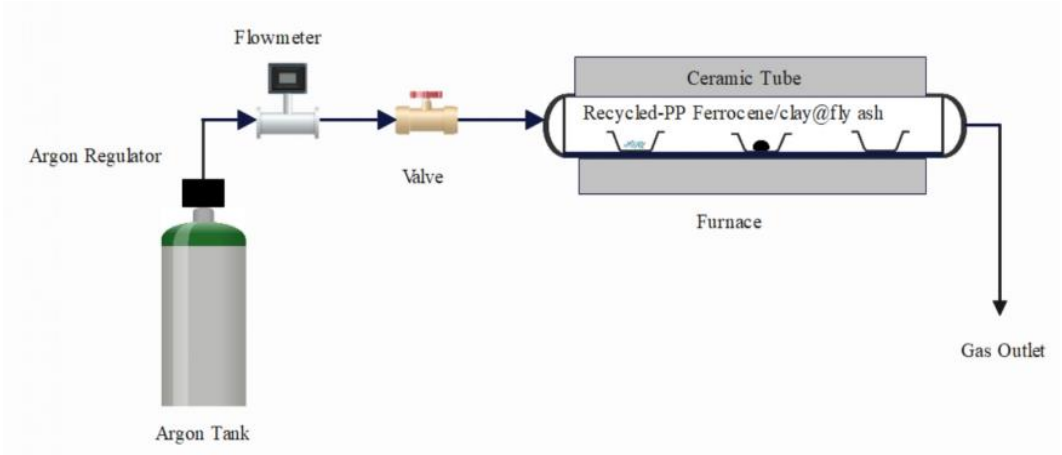

Fig. 1 Schematic diagram of CVD (Chemical Vapour Deposition) reactor setup

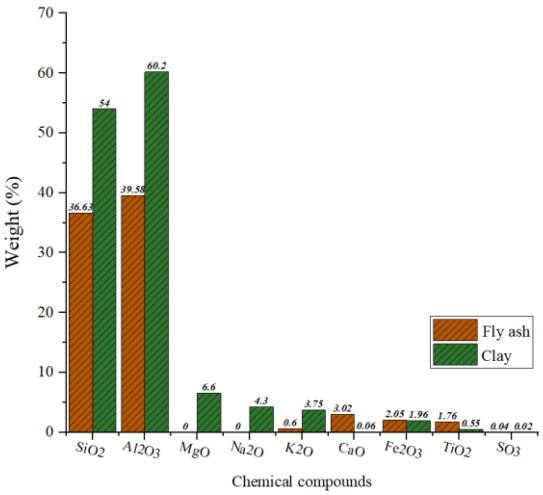

Fig. 2 Chemical compounds of fly ash and clay

minutes to room temperature. The chosen reaction time was based on preliminary studies that had been conducted previously. Subsequently, the boats were carefully taken out from the furnace, and the carbon products were peeled off from the ceramic boats. For control purposes, the thermal decomposition of recycled PP on ferrocene (without substrate) was also conducted to synthesize pristine CNTs.

3.3 Characterisations

The major chemical compound of fly ash and clay was first analysed using an energy-dispersing x-ray fluorescence spectrometer (EDXRF; Thermo Scientific™ ARL™ QUANT'X). The analysis then proceeds using x-ray diffractometers (XRD; D8-ADVANCE, Bruker, Germany) to further identify the phase of crystalline materials that exist in both substrates. After CVD, both substrates were again examined using XRD to identify new compounds produced and also to confirm the formation of CNTs. The morphology of fly ash and clay after CVD was observed from images of scanning electron microscope (VP-SEM; Zeiss SupraTM).

4. Results and discussion

4.1 Compound analysis of fly ash and clay

Major chemical compounds present in fly ash and clay as metal catalyst substrate in this study was revealed by XRF analysis as shown in Fig. 2. Fly ash has a considerable proportion of alumina (Al_2O_3) at 39.58 wt.% and a high percentage of silica (SiO_2) at 36.63 wt.% with low content of calcium oxide (CaO) of 3.02 wt.%. The fly ash can be classified as Class F based on the total weight percentage of SiO_2, Al_2O_3, and ferric oxide (Fe_2O_3) of 78.06%. On the other hand, clay is made up of 60.2 wt.% Al_2O_3 and 54 wt.% SiO_2. Both Al_2O_3 and SiO_2 were proven to positively affectthe growth of CNTs. Al_2O_3 has strong metal-carrier interaction that helps to disperse metal catalysts on

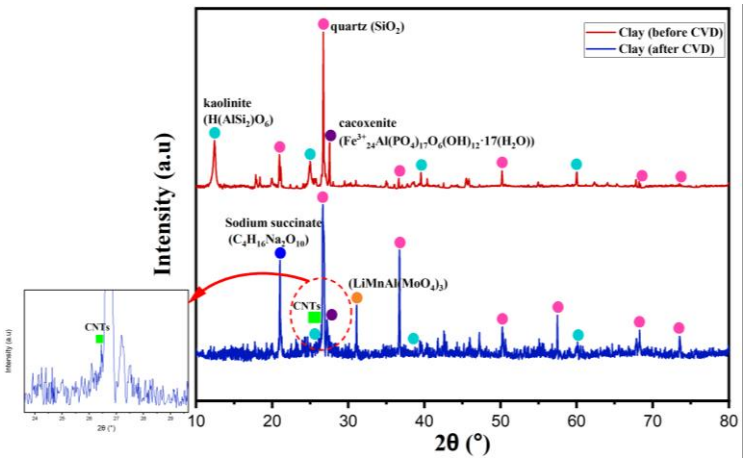

Fig. 3 XRD (X-Ray Diffraction) pattern of clay: Before and after CVD (Chemical Vapour Deposition)

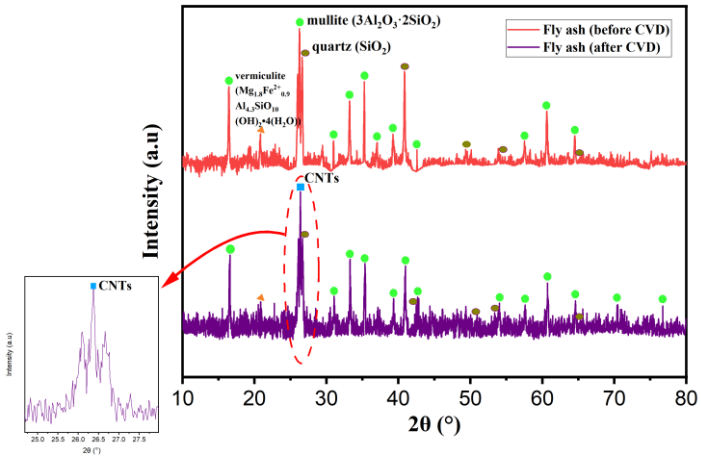

Fig. 4 XRD (X-Ray Diffraction) pattern of fly ash: Before and after CVD (Chemical Vapour Deposition)

their surface and within their pores. Hence provide high catalytic site density (Mattev *et al.* 2008). On the other hand, SiO_2 is capable to prevent the metal catalyst from sintering and collapsing. This provides a dependable open pore structure for CNTs growth. Clay also shows a significant amount of magnesium oxide (MgO), that proven to help to promote the growth of Single-walled carbon nanotubes (SWCNTs) (Xiao-Di *et al.* 2019). All in all, this finding seems promising in the formation of CNTs.

4.2 Analysis of crystal structure of clay: Before and after CVD

Clay originally consists of quartz (SiO_2), kaolinite ($H(AlSi_2)O_6$) and cacoxenite $Fe^{3+}{}_{24}Al(PO_4)_{17}O_6(OH)_{12}\cdot17(H_2O)$ as shown in Fig. 3. Formation of CNTs after CVD is evidenced by the exhibition of the peak at 26.43° with (002) plane (Dunens, MacKenzie and Harris, 2009). In addition, new compounds were formed from the reactions between the original compounds present with deposited carbon or interatomic bonding in clay at high temperatures. The peak at 21.02°

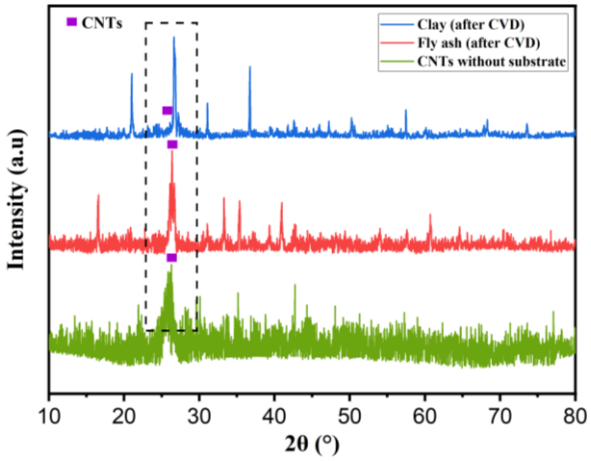

Fig. 5 XRD (X-Ray Diffraction) pattern of clay and fly ash after CVD (Chemical Vapour Deposition) and grown-CNTs (Carbon Nanotubes) without substrate

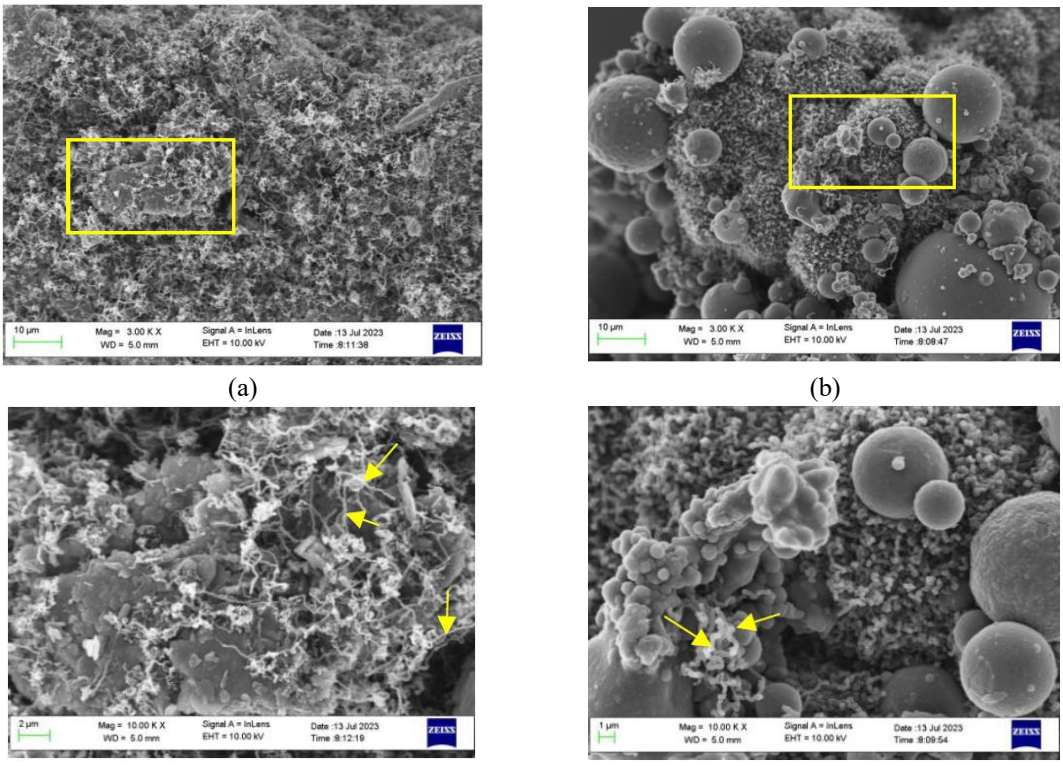

Fig. 6 SEM (Scanning Electron Microscopy) images of (a) Clay, (b) Fly ash after CVD (Chemical Vapour Deposition), (c) and (d) Enlarged area from magnification of 3.0K x to 10K x

indicated the presence of sodium succinate ($C_4H_4Na_2O_4$), while the peak at 36.72° corresponded to lithium manganese aluminum molybdenum oxide ($AlLiMnMo_3O_{12}$).

4.3 Analysis of crystal structure of fly ash: Before and after CVD

The prominent peak at 26.43° which corresponds to the (002) plane, revealed the successful incorporation of CNTs onto its surface as depicted in Fig. 4. After the CVD process, the XRD pattern of the CNTs on fly ash still exhibited significant peaks, particularly mullite ($Al_6O_{13}Si_2$) at 26.35°. Mullite is known to have high thermal stability, which allowed it to retain its structure during the CVD process at 900°C (Ferreira *et al.* 2019).

4.4 Analysis of peak position: CNTs on substrate and CNTs without substrate

The peak positions for both clay and fly ash after the CVD process in Fig. 5 were observed at 26.43°, while the peak for the grown-CNTs without substrate occurred at 26.23°. The shift in the peak position between these two orientations could be attributed to the presence of specific components in the substrates, such as quartz and mullite. These components have an influence on the growth and arrangement of the CNTs during the CVD process (Dunens, MacKenzie and Harris, 2009).

The interaction between the CNTs and fly ash or clay could affect the crystal structure and orientation of the resulting CNTs as a whole. The presence of components like quartz and mullite introduces additional lattice distortion, leading to a slightly different diffraction angle (Amigó *et al.* 2005; Rao, Narayanaswami and Prasad, 2010). As a result, the peak position of CNTs growth without substrate was shifted from 26.23° to 26.43° for the CNTs grown on substrates.

4.5 Morphological analysis of clay and fly ash after CVD

The morphology of clay and fly ash after CVD was analyzed using SEM images, as shown in Fig. 6. The surface of the clay was covered by CNTs, as depicted in Fig. 6(a). However, a closer observation at high magnification (x10K) in Fig. 6(a) revealed the non-uniform distribution of CNTs caused by active Fe particles that were not evenly dispersed on the clay surface. Similar observations were made for the growth of CNTs on fly ash, as illustrated in Fig. 6(b). At low magnification in SEM (Fig. 6(c) and Fig. 6(d), not all surfaces of the fly ash were fully covered by CNTs. The formed fibers were also less refined compared to those on clay. By utilizing Image-J on the SEM images, it was determined that the fibers growing on clay and fly ash had diameters ranging from 80-130 nm and 77-124 nm, respectively. This suggests that some of the fibers were not only in the form of CNTs but also carbon fibers. Further optimization of parameters is necessary to ensure that only CNTs are formed.

5. Conclusions

- XRF analysis indicates that both clay and fly ash primarily consist of alumina and silica, making them suitable for exploitation as substrates in the CVD process. However, while XRD analysis showed the presence of CNTs in the products obtained using both substrates, SEM observations revealed that these CNTs were mixed with carbon fibers, displaying non-uniform diameter and morphology.
- Therefore, optimizing the CVD conditions is highly recommended for future studies. In

summary, clay and fly ash demonstrate potential as feasible substrates for CNT growth.

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