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Synthesis of C₆₀ Nanotube from Pyrolysis of Plastic Waste (Polypropylene) with Catalyst

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Abstract:

Fullerene nanotube was synthesized in this research by pyrolysis of plastic waste Polypropylene (PP) at 1000 ° C for two hours in a closed reactor made from stainless steel using molybdenum oxide (MoO₃) as a catalyst and nitrogen gas. The resultant carbon was purified and characterized by energy dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD). The surface characteristics of C₆₀ nanotubes were observed with the Field emission scanning electron microscopy (FESEM). The carbon is evenly spread and has the highest concentration from SEM-EDX characterization. The result of XRD and FESEM shows that C₆₀ nanotubes are present in Nano figures, synthesized at 1000 ° C and with pyrolysis temperature 400° C. The synthesis operation doing in one reactor and limited time.

Key words: Catalysts, Fullerene Nanotubes, Plastic waste, Polypropylene, Pyrolysis.

Introduction:

Plastic materials are characterized by many properties that make them desirable in practical applications such as low cost, lightness and durability and as a result are necessary for our daily lives (1). Municipal solid waste is non-degradable and is not implemented in nature. It is disposed of by the way known as landfill, which accumulates multiple types of plastic waste. In these tombs there are many microorganisms that accelerate the degradation of organic matter associated with plastic waste (2). In many developing countries, the amount of plastic consumption is much higher than the average global consumption. The large production of plastic poses a major challenge to deal with these huge quantities of plastic waste after use. Plastic materials in solid waste release harmful chemicals in the soil that can then flow into the groundwater or other surrounding rivers and lakes so it can pose a significant risk to the organisms that drink contaminated water (3). Polypropylene is an attractive candidate for packaging applications and has a wide popularity in automobile and electronics field due to its excellent advantages of good thermal stability, chemical resistance, easy handling, good mechanical characteristics and inexpensiveness (4).

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Waste materials from domestic wastes to industrial remains, rise harmful effects on environmental and human health regarded as a source of air, soil, water and marine pollution. However, wastes can be used as tools to produce useful goods. A significant technique to obtain this goal is pyrolysis. Pyrolysis relates to thermal decomposition that is operated in an air-free condition (5). Pyrolysis is a probable alternative to landfill for processing plastic waste, resulting decomposition products which can be used as " fuels instead of gas, diesel or fuel oils" (6). Additionally, pyrolysis of plastics has also been utilized to manufacture various types of Nano Carbon such as nanotubes, nanofiber, Nano rods, nanowires, etc., C₆₀ nanotube which have high value and exceptional physical and chemical properties because of their impressive characteristic like high surface area, porous-rich structure, high conductivity and excellent chemical stability, by blending plastics and catalyst in one reactor (7). The properties of carbon nanotubes and the percentage of the product depend mainly on raw materials. For instance, various methods have been developed to produce CNTs such as arc discharge, pyrolysis, laser ablation of carbon, plasma assisted deposition and chemical vapor deposition (CVD) (8-10). Fullerene is any molecule in the form of an ellipsoid, tubular or a hollow sphere structure composed entirely of carbon. They are generally referred to as "Buckyballs" (11). There are many

types of fullerene such as C_{60} rods and C_{60} tubes (12).

The research objectives are to increase the economic value to benefit from plastics waste and assist in addressing environmental problems associated with this waste and produce new nanomaterials that enter into the technological industry.

Materials and Method:

Waste of polypropylene, collected from local grocery stores, the catalyst MoO_3 (98%) purchased from (BDH company), H_2SO_4 (98%) purchased from (BDH company), $MgSO_4$ (98%) purchased from (BDH company), pyrogallol (99%) purchased from (Honeywell Riedel-de Haën) and nitrogen gas (local).

Preparation of system gas

The nitrogen gas bottle was connected to three traps, the first trap contained concentrated sulfuric acid (H_2SO_4), which absorbed water from the gas, then the gas was passed to the second trap which contained a saturated solution of pyrogallol to absorb oxygen from the gas, finally the gas was passed to the magnesium sulphate ($MgSO_4$) to absorb the rest of the acid. Then the gas was passed to the reactor system through a trap.

Methods

The samples were washed, air-dried and shredded into small pieces of an area that's around 1mm^2 . 25 g of shredded PP was placed inside a stainless-steel reactor that is filled with some inert gas (nitrogen) at low pressure (between 50 and 70 mbar). 0.5 g of (MoO_3) catalyst was placed in tube nozzle connected with reactor. The reactor was tightly closed and put in an electric furnace to be heated as shown in Fig.1. This reactor is connected to condenser and then to three neck round-bottom flask for products collection. Nitrogen gas was pumped at 25°C until the temperature reached 500°C . The temperature of the furnace was gradually raised. When the temperature of 400°C was reached and the wastes began to decompose, the catalyst was added from the tube nozzle. At this level the distillation process began and at the end of distillation the temperature was raised to required temperature. We used 1000°C for two hours, at a heating ramp rate of $13^\circ\text{C}/\text{min}$, then allowed to cool to room temperature naturally. It was found that the final product in the reactor included carbon powder.

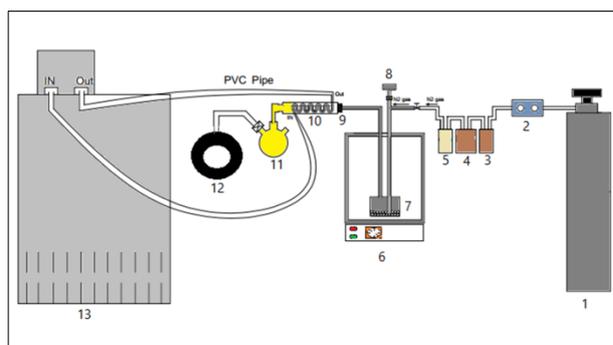


Figure 1. Schematic diagram of unit used for synthesizing C_{60} nanotubes by pyrolysis method. In this diagram, 1) gas N_2 cylinder, 2) Valve, 3) concentrated sulfuric acid (H_2SO_4), 4) Saturated solution of pyrogallol, 5) Magnesium sulphate ($MgSO_4$), 6) Electric furnace, 7) Stainless steel reactor, 8) tube nozzle containing catalyst, 9) Rubber, 10) Condenser, 11) three neck round-bottom flask, 12) Rubber bag to collect the resultant gas, 13) Water bath.

Carbon Nanotube Identification

The following equipments were used to identify C_{60} nanotubes properties:

Field Emission Scanning Electron Microscopy (FE-SEM)

The morphology and size of samples were studied by scanning electron microscopy (SEM; FEG-SEM MIRA3 TESCAN, Czech Republic), which is configured to operate at (15.0 kV) various magnification level.

X-Ray Diffraction (XRD)

The X-ray diffraction (XRD, X'PERT PRO from Philips, Netherlands) was evaluated to determine the crystal structure and phase the samples, with $Cu-K\alpha$ radiation ($\lambda=1.54178 \text{ \AA}$), operated at 40 kV and 40 mA, was measured in 2θ range from 10° to 80° , performed on a University of Kashan (Iran).

Energy Dispersive X-Ray Analysis (EDS)

The elemental composition of samples was studied by (EDS, MIRA3 TESCAN, Czech Republic)

Results and Discussion:

Figure 2A shows the XRD patterns of the PP pyrolysis at 1000°C without catalyst and having the diffraction peaks at the value of 23° , 28.5° and 43° were ascribed to the (002), (100) and (101) reflections. Figure 2B shows the XRD patterns of the C_{60} nanotubes from waste PP with MoO_3 , the diffraction peaks at the value of 23° , 28.5° and 43° were ascribed to the (002), (100) and (101) reflections, respectively of the CNTs (JCPDS PDF no. 41-1487) (13-15), MoO_3 has diffraction peaks at 33.5° , 35.4° , 39.0° , 49.2° , 55.1° , 58.8° ,

64.5°, 69.5° and 78.9° corresponding to the (111), (041), (051), (200), (211), (042), (081), (062), and (202) reflection planes assigned to the orthorhombic phase of MoO₃ (JCPDS PDF no. 85-2405) (16). The XRD patterns of the MoO₃/C₆₀NTs hybrid are shown in Fig.2B excluding the characteristic C₆₀NTs (002), (100) and (101) peaks, all the other peaks could be indexed to the orthorhombic phase of MoO₃, revealing that MoO₃ had been incorporated into the MoO₃/C₆₀NTs hybrid sample.

The other peaks notices refer to the additives of polymer and the substrate used in the measurement (17-18)

Average crystal size in the product that can be found using X-ray diffraction profile. Calculating the crystal size (D) can be done by using the Debye Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where *K* is the Scherrer constant, λ is the wavelength of light used for the diffraction, β is the full width at half maximum of the sharp peaks and θ is the angle measured. The Scherrer constant (*k*) in

the above formula accounts for the shape of the particle and is generally taken to have the value 0.9 (19).

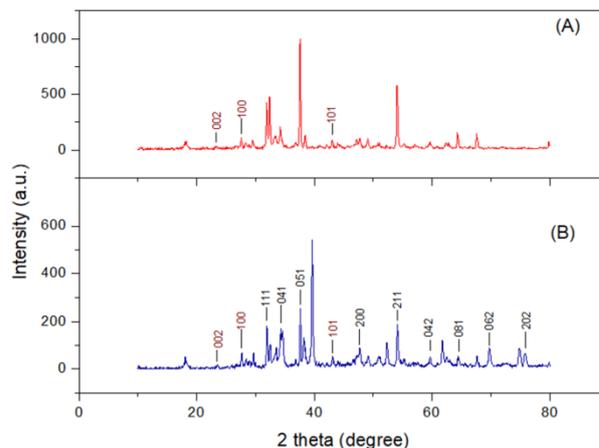


Figure 2. XRD Pattern of the C₆₀NTs. (A) PP without catalyst at 1000 °C for two hours of pyrolysis. (B) PP with catalyst MoO₃ at 1000 °C for two hours of pyrolysis.

Table 1. Structural parameter of Carbon Nanostructure (C₆₀NTs) from PP, (JCPDS Database, card NO. 41-1487).

2θ (deg)	FWHM (deg)	Cos θ	FWHM (rad)	hkl	Crystalline Size (nm)
23	0.09	0.978736458	0.001570681	002	90.33474
28.5	0.09	0.967327878	0.001570681	100	91.4
43	0.1208	0.930117812	0.002108202	101	70.8

From Table1, we could calculate the average crystal size of C₆₀NTs as shown below:

Average crystal size = 84.17 nm.

The morphology of the sample was revealed by FESEM. Figure 3-A shows a typical FESEM

image of the sample. It is found that large quantities of nanostructures (C₆₀NTs) were obtained (12). These nanotubes are carbon (34.5-90.6) nm in diameter, and a few micrometers in length, as shown in Fig. 3-B.

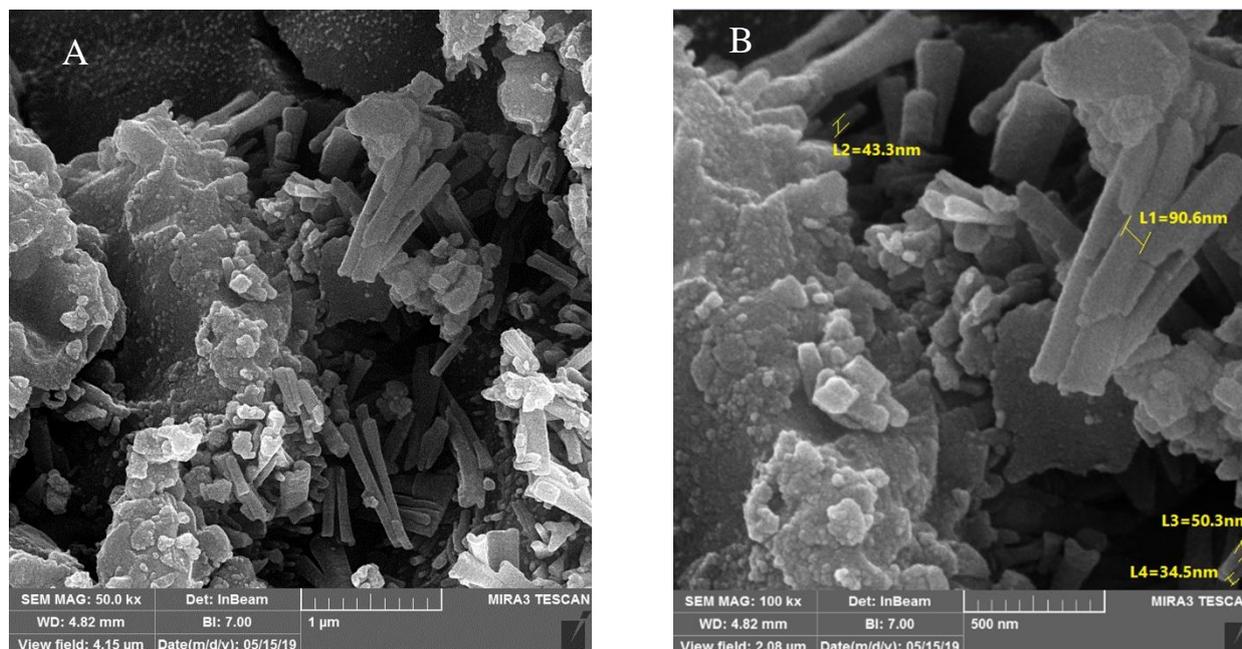


Figure 3. FE- SEM image of C₆₀nanotubes grown on MoO₃ (A): 1 µm (B): 500 nm

Figure 4 shows the high concentration of the carbon content which indicates high purity, and shows the amount of catalyst used in pyrolysis (20). The other elements noticed (Au, Si, Al and Cl) refer to the elements in standard in analysis device (21-22), and the other components (K, Ca and Na) are additives to improve properties of polymer.

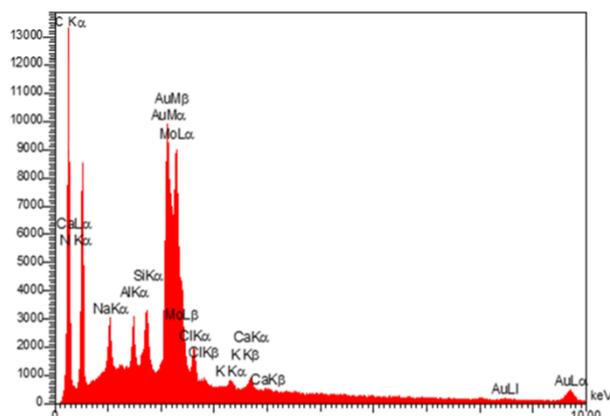


Figure 4. EDS spectra of C₆₀ nanotube with MoO₃ at 1000°C for two hours of pyrolysis

Conclusions:

CNT is successfully synthesized via a new experimental method by using one pyrolysis reactor of polypropylene at 400°C for about 30 minutes and decomposed the polymer chains at 1000°C for two hours with nitrogen ambiance. Resulting of XRD and FESEM shows there is carbon nanostructure at this temperature and marked by a peak intensity at $2\theta = 23^\circ, 28.5^\circ$ and 43° . Moreover, the result of EDX shows that carbon is highest spread when compared with the others.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of AL-Anbar.

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تحضير أنابيب الفوليرين النانوية من الأنحلال الحراري للمخلفات البلاستيكية (بولي بروبيلين) مع العامل المساعد

ابراهيم جليل ابراهيم

امال شاكر عبود

قسم الكيمياء، كلية العلوم، جامعة الانبار، الانبار، العراق

الخلاصة:

في هذا البحث تم تصنيع الفوليرين من نوع أنابيب نانوية عن طريق الانحلال الحراري للنفايات البلاستيكية (البولي بروبيلين) عند درجة حرارة 1000 درجة مئوية لمدة ساعتين في مفاعل مغلق مصنوع من الفولاذ المقاوم للصدأ باستخدام أكسيد الموليبيديوم (MoO₃) كعامل مساعد وغاز النيتروجين. تمت تنقية الكربون الناتج وتشخيصه باستخدام التحليل الطيفي للأشعة السينية (EDS)، حيود الأشعة السينية. وقد لوحظت الخصائص السطحية للفوليرين من نوع أنابيب نانوية باستخدام المجهر الإلكتروني الماسح (FESEM). ينتشر الكربون بالتساوي ويحتوي على أعلى تركيز من خلال تشخيص SEM-EDX. تظهر نتيجة حيود الأشعة السينية و المجهر الإلكتروني الماسح ان الفوليرين من نوع أنابيب نانوية موجود في أشكال نانوية، يتم تصنيعها عند 1000 درجة مئوية و مع درجة الأنحلال الحراري 400 درجة مئوية. عملية التحضير تتم في مفاعل واحد و وقت محدود.

الكلمات المفتاحية: عوامل مساعدة، أنابيب فوليرين نانوية، مخلفات بلاستيكية، بولي بروبيلين، الانحلال الحراري.