SYNTHESIS OF NANO-CARBONS FROM DIFFERENT WASTE PLASTICS AND DIVERSE CATALYSTS

A Thesis Presented

By

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ABSTRACT

Polymers have important and widespread applications in modern materials due to their excellent formability, chemical stability, light weight and low cost. Their production has increased exponentially over the last 60 years after their introduction to the markets from 1.5 million tons/year in 1950 to 322 million tons per year in 2015. Polymeric materials are often discarded after a single use, and post-consumer waste has become a very serious environmental problem, as it is non-biodegradable. Therefore, different recycling, reuse and, even upcycling methods for waste plastics have been investigated. This research aimed at systematically investigating the influence of the types of stainless steel catalysts and their pretreatment on the formation of nanotubes. The targeted polymer feedstocks were post-consumer polyethylene (PE), polyethylene terephthalate (PETE), polypropylene (PP) and polystyrene (PS) as pellets, clippings or powders. The polymers were pyrolyzed in an inert nitrogen atmosphere in an electrically heated furnace kept at 800 °C. Their effluent gases from this furnace, containing the gaseous pyrolyzates of the polymers, were then channeled to a separate electrically-heated furnace, were the catalyst substrates were heated to 800 °C. Therein synthesis of carbon nanotubes took place by chemical vapor deposition (CVD) in nitrogen. The catalytic substrates used for the nanoparticle growth were T304, T316, and T316L stainless steel meshes. The substrates were used as received, or pretreated by acid wash and/or heat-treated in air or in nitrogen at 800 °C. The produced nanomaterials were characterized by the use of SEM and TEM.

Keywords: Polymer, Environment, Carbon Nanotubes, Pyrolysis, Waste plastic
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Chapter 1

(Introduction)

Energy consumption:

Energy demand has been increasing rapidly from the industrial revolution. Fossil fuels such as coal, natural gas, and petroleum have been considered as the main energy resources in modern times. Coal plays an important role in the power generation, and nearly 40% of electricity is currently generated by coal in the world [1]. Due to increasing amounts of greenhouse gasses in the atmosphere [2-6], an emerging challenge in the 21st Century is to identify alternative fuels that can partially replace fossil fuels. This issue has motivated researchers to examine the feasibility of utilization of renewable fuels in utility and industrial furnaces. Biomass is an attractive renewable energy source [7-11]. Also, alternative fuels can be found in municipal/industrial recycling and waste streams. Post-consumer plastics is one of those materials that has been studied extensively as an alternative fuel at Northeastern University’s Combustion & Air Pollution laboratory [12-19].

Plastics and plastic waste:

Plastics, which are a man-made materials with long chain polymeric molecules [20], have become one of the most important materials in human’s daily utilization since the 1940s [21] because of their chemical stability, formability and low cost [22-24]. The compound annual growth rate of plastics production is about 8.6% from 1950 to 2015, see Fig 1. The
distribution of plastics production is shown in Fig 2 where it can be seen that China, Europe, and North America were the top three plastics producers in the world in the year 2015 [25].

**Figure 1** World plastics production 1950 – 2015 [25].

- Plastics are a global success story.
- Continuous growth for more than 50 years.
- Plastics production ramped up from 1.5 Mio. t in 1950 to ~322 Mio. t in 2015. In 2015 global plastic's production grew by 3.4% compared to 2014.
- Compound Annual Growth Rate (CAGR) from 1950 to 2015 is about 8.6%.

**Figure 2** World plastics production by area 2006 – 2015 [25].

- Asia with the leading country China (28%) mean-while accounts for more than 49% of worldwide production.
- Europe and NAFTA are on a similar level each with a share of around 18%–19%.
- Within a few years, China has risen to the most important plastics producer. All other regions lost global production shares.
There are many different types of plastics, which are defined by their chemical composition. Different plastics have different properties, and this makes them have different application fields. Fig 3 shows that polyethylene (LDPE and HDPE) and polypropylene (PP) are most commonly used. Plastics find widespread applications and since, their production is of low cost they are often discarded upon single use, generating voluminous wasted.

Since plastics resist natural degradation, the plastic wastes increase is a serious environmental problem, contributing to air pollution [26], soil pollution and marine pollution [27-29]. Landfilling, incineration, and recycling are three common methods to deal with plastic waste. Plastic landfilling will lead a very serious soil pollution and reduce the available land space for humans, as illustrated in Fig 4 a [30]. Uncontrolled open-air
burning of wastes plastics, shown in Fig 4 b, generates air pollution because of incomplete combustion [26] and may produce some toxic matters like dioxins.

(a) 
(b) 

Figure 4 Harmful plastic treatment method (a) landfilling, (b) burning

Recycling is considered as an environment-friendly method to dispose of the plastic waste. Recycling also can help to improve the efficiency of using petroleum. Biological recycling of biodegradable plastics is degrading of the waste plastic by microorganisms [30-35]. Mechanical methods are used to collect, re-manufacture waste plastic without any chemical changes [21, 36-38]. Some chemical processes, such as pyrolysis, are used to decompose plastic into hydrocarbon, hydrogen and some other monomers or compounds. The rate of recycling waste plastic has increased in recent years, as shown in Fig 5. However, landfilling still possesses a definite proportion. Finding different applications to recycle the waste plastic is also very important. There are some researches that use the pyrolyzates as fuel [39, 40]. This applications can be considered as an alternative energy resource to reduce the pressure of using fossil fuel. The pyrolyzates from the chemical recycling of waste plastic has also important applications, such as generating gaseous and liquid fuels [39, 40] [41-46] and carbon nanotubes (CNTs) [12-16].
Figure 5 Total plastics waste and recovery 2006 – 2014 [25]

What are Carbon Nanotubes?

Iijima [47] first discovered CNTs in 1991. CNT is a micrometer-scale graphene sheet rolled into a cylinder of nanoscale diameter and capped with spherical fullerene molecules [48]. CNTs have excellent thermal and electrical conductivity, high tensile strength, thermal and chemical stability and some other physical and chemical properties [49-60] which make CNTs is one of the most applicable nanomaterials in the last two decades. CNTs have a wide range of potential application in composite materials, microelectronics, electrochemistry (batteries and solar cell) and biological field [61-80]. Laser ablation of carbon [81-83], carbon-arc discharge [47, 76, 84-86] and chemical vapor deposition (CVD) [87-89] are three usual methods to generate CNTs. Purification and non-limitation of the sample size make CVD more popular than the other two methods to generate CNTs [90]. The carbonaceous feedstock to generate CNT by CVD comprise a wide range of hydrocarbons, such as C₂H₂, CH₄, benzene, etc. [91-95].
Previous work on post-consumer plastics:

The carbonaceous gas is used by the CVD process as a carbon donor for the generation of the CNTs. The concept of synthesis of CNT from plastic waste has been ongoing since 1996 [96] because the most of the plastic pyrolyzation is a mixture of hydrocarbons (gas phase and liquid phase) [97-101]. In recent years there have been many attempts at pyrolysis of different plastics such as polyethylene [102-105], polypropylene [102, 105, 106], polystyrene [107, 108], polyethylene terephthalate [109, 110] and different mixtures of plastics [111, 112]. The pyrolysis products of plastics then can be used a carbon growth agents for CNTs [19].

Previous work on Catalysts:

Selecting an appropriate catalyst is the most challenging part of generating CNT in CVD. Metals such as nickel, iron and cobalt, as well as metallic compounds such as nickel oxides, cobalt acetate, etc., have been used as a catalyst in the literature [93, 113-122]. Moreover, stainless steels (types 304,316,316L) have been reported as feasible catalysts in CNT synthesis from hydrocarbon carbon donors, such as C₂H₂, C₆H₆ and C₂H₆ [123-128] . A review of the literature shows that there have been many attempts at improving the CNT generation by using different pre-treatment methods [123, 125, 129-135] .

In the previous work in this laboratory, Zhuo et al. [136] have focused on the heat treatment of stainless steel T316L to improve the CNT yield. Their heat treatment method improved the CNT yield by 1.45%. Martínez-Hansen et al. [126] have used three steps of pre-treatment including acid wash, oxidation by air and heat treating in H₂ to pre-treat the T316L stainless steel. This method improved the yield by 2%. Baddour et al. [127] have
applied a combination of washing the T304 stainless steel in acetone or acids and heat treating in N₂. Using this method, they reported 97% coverage of the catalyst with CNTs.

The goal of this research:

Previous research in this laboratory has been performed on the synthesis of CNTs from a number of post-consumer plastics [12-16, 19, 137]. However, additional work was deemed necessary on the selection of the right catalyst substrate and its appropriate pre-treatment method in view of the work of Baddour et al. [127] and Zhuo et al. [136] to maximize the CNT yield per unit area of catalyst. This was accomplished by applying different pre-treatment methods on stainless steel meshes of three different types 304, 316 and 316L to investigate their capability to generate CNT and thus obtain the maximum yield from different post-consumer plastics. The targeted polymers were polyethylene (PE), polyethylene terephthalate (PETE), polypropylene (PP) and polystyrene (PS) in the size range of a few millimeter pellets, powders, and debris. Considering difficulties of the waste plastic separation into different categories in the recycling process, in this study, a mixture of the aforesaid waste plastics, in equal proportions by mass, was also tested as a feedstock for CNT generation on the stainless steel types 304, 316 and 316L.
Chapter 2
Comparison of different pre-treatment methods for different catalysts to generate CNT from polyethylene

2.1 Methods

2.1.1 Preparation of samples

Three different stainless steel (T304, T316 and T316L) meshes, procured from TWP Inc. (T304 and T316) and Huaxin Hardware Inc. (T316L), were used as catalysts and the chemical compositions are shown in Table 1. There it can be seen that T316 and T316L have more Ni and less Cr than T304; moreover T304 doesn't have any Mo. T316L have less Carbon than T316. All of the stainless steel mesh has the same size (400 per inch). The meshes were cut into circular coupons with diameters of 38mm. The stainless steel meshes were washed with isopropyl alcohol in an ultrasonic bath and, then, they were subjected to different pretreatment methods. A fixed amount of 4 g of polyethylene was used in the experiment as the feedstock. N\textsubscript{2} which was procured from Medical-Technical Gases Inc. was used as carrier gas and protection gas at the flow rate of 2 l/min.

<table>
<thead>
<tr>
<th>Grade (wt. %)</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>0.08</td>
<td>1</td>
<td>2</td>
<td>0.045</td>
<td>0.03</td>
<td>8-10.5</td>
<td>18-20</td>
<td>/</td>
</tr>
<tr>
<td>316</td>
<td>0.08</td>
<td>1</td>
<td>2</td>
<td>0.045</td>
<td>0.03</td>
<td>10.0-14.0</td>
<td>16-18</td>
<td>2.00-3.00</td>
</tr>
<tr>
<td>316L</td>
<td>0.03</td>
<td>1</td>
<td>2</td>
<td>0.045</td>
<td>0.03</td>
<td>12.0-15.0</td>
<td>16-18</td>
<td>2.00-3.00</td>
</tr>
</tbody>
</table>

2.1.2 Experimental Apparatus

A specially designed quartz tube which is shown in Fig 6 was fitted inside two electrically-heated furnace, from HEVI-DUTY ELECTRIC Co. The ceramic honeycomb filter which is
manufactured by *Ibiden* was used to prevent 97% soot that generated by pyrolysis process [19]. The experiment procedure included two steps. The first step was pyrolysis and the second step was CNT synthesis. For the pyrolysis process, Furnace 1 was preheated up to 800 °C and then a ceramic boat containing a certain mass of polymer was inserted into the quartz tube in an inert N₂ flow. The polymer was pyrolyzed into a gaseous hydrocarbon mixture. The gaseous effluent then traversed the ceramic filter and transitioned into the second step, the synthesis process. Furnace 2 was also heated up to 800°C. When the gaseous mixture traversed the treated catalyst meshes, which were placed at the center of Furnace 2, the CNTs was generated at the surface of the catalyst by Chemical Vapor Deposition (CVD).

Scanning electron microscope (SEM) was used to observe the surface of the stainless steel. SEM (*Hitachi S-4800*) was used in these experiments to observe the coverage of the CNT. The instrument was operated with a 3 kV of accelerating voltage, 10 µA of beam current and 8.2 mm working distance.

![Figure 6 Sketch of the experiment apparatus](image-url)

### 2.2 Experimental Results
Four pre-treatment methods which, are described in Table 2, were used to generate CNTs. Three different types of stainless steel meshes (T304, T316 and T316L) were used in these experiments.

**Table 2** Pre-treatment methods and the marks

<table>
<thead>
<tr>
<th>Pre-treatment method</th>
<th>label</th>
</tr>
</thead>
<tbody>
<tr>
<td>No pre-treatment</td>
<td>a</td>
</tr>
<tr>
<td>Acid (40% HCl) wash for 10 minutes</td>
<td>b</td>
</tr>
<tr>
<td>Heat treatment in air at 800°C for 1 minute then quench</td>
<td>c</td>
</tr>
<tr>
<td>Acid (HCl) wash for 10 minutes then heat treatment in air at 800°C for 1 minute and quench</td>
<td>d</td>
</tr>
<tr>
<td>Acid (HCl) wash for 10 minutes then heat treatment in N2 at 800°C for 30 min</td>
<td>e</td>
</tr>
</tbody>
</table>

Fig 7 shows the yield of CNTs from pyrolysis of 4 g polyethylene feedstock. The yield is:

\[
\text{Yield} = \frac{\text{Mass of CNT}}{\text{Mass of Catalysts}} \times 100\% \quad (1)
\]

![Yield of CNT by different pre-treatment methods](image)

**Figure 7.** The yield of CNT on different stainless steel catalyst meshes prepared by different pre-treatment methods a, b, c, d and e, which are described in Table 2.
2.3 Discussion

Fig 7 shows the yield of CNTs on the stainless steel catalyst substrates prepared by different pre-treatment methods. The purpose of pre-treatment was to break the chromium oxide layer at the surface of the stainless steel, to increase the surface roughness and to activate the surface to act as a catalyst for CNT growth [136]. Figs. 8 a, b and c show SEM photos of the original untreated surfaces of the three steels used in this investigation. Figs. 8 d, e and f show the three steel surfaces after acid wash. It can be detected from Figs. 8 d, e and f that the surface of T304 was affected the most by the Cl-ion environment generated by the HCl acid, whereas T316 and T316 L were not visibly affected. This difference is attributed to the fact that both T316 and T316L contain Mo element, which is known to resist corrosion [138]. Acid wash can help to remove lipids and oxides from the surface of the stainless steel, which can expose the metal alloy and promote the growth of CNT and increase their yields, as shown in Fig. 7. Heat treatment in air was effective to alter the surfaces of all types of stainless steel, as shown in Figs. 8 g, h and i. The effect of heat treatment in air generated some nanoscale morphologies on the surfaces of the stainless steel substrates, with grain size in the order of 50 nm. Figs. 8 j, k and l show the effects the acid wash superimposed on heat treatment in air. Clearly the combined treatments promoted the generation of bigger and more regular nanoscale morphologies, with grain size in the order of 160 nm. The resulting substrates facilitated the synthesis of larger quantities of CNTs than the case of heat treated in air alone, as attested by the yields displayed in Fig. 7.
The effects of exposing the acid-treated samples to additional heat treatment in air or in nitrogen are shown in Figs. 8 g, h, i, j, k, l, m, n and o. On one hand, the effects of superimposing acid treatment to the heat treatment in air altered the surfaces of the T304 and T316 the most, but had little effect on the surface of the heat treated T316L. On the other hand, the effects of superimposing acid treatment to the heat treatment in nitrogen altered the surfaces of all steels. It becomes apparent by comparing Figs. 8 j, k and l and Figs. 8 m, n and o that the surfaces of the steels exposed to air and nitrogen contained grains of distinctly different types and shapes, the former containing spheroidal grains, the latter more elongated rice-shaped grains. Given that the product CNT yields on the air treated substrates was consistently higher than those in nitrogen, see Fig. 7, it can be concluded that air was more successful to break the protective chromium oxide layer of the stainless steel substrates, as also reported in Ref. [136].
Figure 8 The SEM pictures of the surfaces by different pre-treatment methods
Chapter 3
Comparison of different catalysts and waste plastics to generate CNTs

3.1 Methods

3.1.1 Preparation of samples

Four common polymers (PE, PETE, PP and PS plastics) and their mixtures are used as feedstock. The chemical composition of these polymers is shown in Table 3. In all experiments, the mass of polymers was fixed (4 g of each plastic and 12 g of the plastic mixture). Three different stainless steel (T304, T316 and 316L) meshes, which are shown in Fig 9, were used as catalysts. All of the stainless steel meshes had the same size (400 per inch). The mesh wires had a diameter of 25 μm. The meshes were cut into circular coupons with diameters of 38 mm. The coupons were first ultra-sonically washed with isopropyl alcohol for 10 min and then they were treated with hydrochloric acid (40 vol% HCl) for 10 min, and were heat treated in air at 800 C for 1 min and then air quenched. The polymers were pyrolyzed in N₂, which was procured from Medical-Technical Gases Inc. at a flow rate of 2 l/min.

<table>
<thead>
<tr>
<th>Type of polymer</th>
<th>Molecular formula</th>
<th>C wt%</th>
<th>H wt</th>
<th>O wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>Polyethylene</td>
<td>(C₂H₄)ₙ</td>
<td>85.7%</td>
<td>14.3%</td>
</tr>
<tr>
<td>PETE</td>
<td>Polyethylene terephthalate</td>
<td>(C₁₀H₈O₄)ₙ</td>
<td>62.5%</td>
<td>4.17%</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
<td>(C₈H₈)ₙ</td>
<td>92.3%</td>
<td>7.7%</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
<td>(C₃H₆)ₙ</td>
<td>85.7%</td>
<td>14.3%</td>
</tr>
</tbody>
</table>
3.1.2 Experimental Apparatus

A specially designed quartz tube which is shown in Fig 6 was fitted inside two electrically-heated furnace, from HEVI-DUTY ELECTRIC Co. A ceramic honeycomb filter, which was manufactured by Ibiden, was used to prevent 97% of any soot generated during the pyrolysis process from entering the CNT synthesis chamber [19]. The experimental procedures included two steps. The first step was pyrolysis and the second step was CNT synthesis. Both steps were conducted in an inert nitrogen environment. For the pyrolysis process, the first furnace was heated up to 800 °C, and then a ceramic boat containing a certain mass of polymer was inserted into the quartz tube. The polymer was pyrolyzed into a gaseous hydrocarbon mixture. The gaseous pyrolyzated then crossed the ceramic filter and transitied into the second step, the CNT synthesis process inside the second furnace, which was also heated to 800°C. When the gaseous mixture crossed the treated catalyst
substrates, placed in the mid-length of the second furnace, the CNTs were generated at the surface of the catalyst mesh wires by Chemical Vapor Deposition (CVD).

Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to observe the generated CNTs. A Hitachi S-4800 SEM instrument, operated at 3 kV of accelerating voltage, 10 µA of beam current and 8.0 mm working distance, was used to observe the coverage of the mesh with CNTs. Upon completion of experiments, the CNTs were removed from the stainless steel mesh by sonication in 100% ethanol. A TEM (JEOL 1010 instrument) was used to detect the qualities and properties of CNTs, with 60-65 kV accelerating voltage and 60 µA beam current. *ImageJ*, an image analysis software by NIH, was used to measure all the CNT parameters.

### 3.2 Experimental Results

In these experiments the following amounts of polymers were pyrolyzed: 4 g of PE, PP, PS and PETE, as well as 12 g of mixtures of the four polymers in equal amounts.

For PE, PP and PS, the pyrolysis yields:

\[
(C_xH_y)_n \rightarrow C_aH_b + H_2
\]  
(1)

For PETE, the pyrolysis yields:

\[
(C_{10}H_8O_4)_m \rightarrow C_aH_b + CO + CO_2 + H_2 + H_2O
\]  
(2)

For the plastic mixture, the pyrolysis yields:

\[
(C_xH_y)_n + (C_{10}H_8O_4)_m \rightarrow C_aH_b + C_2H_6O_2C + CO + CO_2 + H_2 + H_2O
\]  
(3)

For all plastics, the Chemical Vapor Deposition procedure yields:
$C_aH_b \rightarrow C + H_2$ \hspace{1cm} (4)

### 3.2.1 Polyethylene

Fig 10 shows SEM and TEM pictures of CNTs grown on the catalytic substrates of T304, T316 and T316L by pyrolysis of polyethylene (PE) feedstock. The SEM pictures show that forests of CNTs were grown on all substrates, around the surfaces of the woven cloth wires. CNT forests on T316 and T316L appear to be denser and the tubes appear to be longer than the CNTs grown on T304. CNT forest density and length are two important factors that impact the yield of the CNTs, which is shown in Fig 11 a. The SEM pictures also show that the CNTs on T304 and T316 are ordered, vertically grown from the curved wire surfaces, whereas the CNT at T316L appear to be relatively unordered. Fig 11 b also shows the measured diameter and thickness (outer diameter – inner diameter) of the CNT at different catalysts. From the table, the CNT yield on T316 is the highest, followed by that on T316L, and then by that on T304. The tube thickness and diameter are the similarities between different catalysts.


**Figure 10** SEM and TEM photographs of CNTs grown on different catalysts from PE feedstock
Figure 11 The (a) yield and (b) physical parameters of CNTs from PE pyrolyzates.
3.2.2 Polypropylene

Fig 12 shows SEM and TEM pictures of CNTs grown on T304, T316 and T316L catalytic substrates by pyrolyzing polypropylene (PP) feedstock. The CNTs that were generated from PP are very similar to the CNTs generated from PE. Again the CNTs generated on T316 and T316L are longer and more densely-populated than the CNTs generated on T304; the CNT generated on T304 and T316 are ordered appear to be vertically grown from the wire surfaces, forming forests, whereas those grown on the T316L are relatively unordered. Fig 13 shows the yield and qualities of the CNT.

**Figure 12** SEM and TEM photographs of CNT grown on different catalysts from PP feedstock
Figure 13 The (a) yield and (b) physical parameters of CNTs from PP pyrolyzates.
3.2.3 Polystyrene

Figure 14 shows SEM and TEM pictures of CNTs grown on T304, T316 and T316L catalytic substrates by pyrolyzing polystyrene (PS) feedstock. Only the CNTs grown on T316 are relatively densely populated and have the appearance of a forest. The CNTs grown on T316L and T304 are sparse and unordered. Fig 15 a shows that the yields of CNTs from PS pyrolyzates are lower than the yields of CNTs from both PP and PE pyrolyzates. The pyrolyzates of polypropylene are composed of nearly 30% of liquid oil, which contain styrene [139]. The oil fraction of the pyrolyzates is not utilized in the generation of CNTs, hence the lower yields. Fig 15 b shows physical parameters of the CNTs that are generated form PS feedstock.

![Figure 14 SEM and TEM photographs of CNT grown on different catalysts from PS feedstock](image-url)
Figure 15 The (a) yield and (b) physical parameters of CNT from PS pyrolyzates
3.2.4 Polyethylene terephthalate

Fig 16 shows SEM and TEM photographs of CNTs grown on the surfaces of T304, T316 and T316L catalyst substrates by pyrolyzing polyethylene terephthalate (PETE) feedstock. No CNTs were grown on T304, hence this catalyst is not included in this figure. The CNTs on T316 and T316L are sparse and unordered. The yields of CNT from PETE pyrolyzates, shown in Fig 17 a, were much lower than those obtained from the other polymers. This was partly attributed to the fact that the pyrolyzates of PETE contain large amounts of CO and CO$_2$ and large amounts of solids and liquids that cannot be utilized for CNT synthesis; also the pyrolyzates of PETE contain benzoic acid that has been reported to be poisonous to the catalyst, and thus, to prevent CNT growth [92, 110]. Fig 17 b also shows physical parameters of the CNTs that were obtained for pyrolysis of PETE.

![SEM and TEM photographs of CNT grown on different catalysts from PETE feedstock](image)

**Figure 16** SEM and TEM photographs of CNT grown on different catalysts from PETE feedstock
Figure 17 The (a) yield and (b) physical parameters of CNT by pyrolysis of PETE.
3.2.5 Mixed Polymers

In practice a lot of postconsumer plastics are collected in mixed form, therefore generation of CNTs from mixed plastics was also examined. Fig 18 shows SEM and TEM photographs of CNTs grown on T304, T316 and T316L substrates from pyrolysis of 12 g mixed plastics feedstock, containing equal amounts of PE, PP, PS and PETE (4 g each). Fig 19 shows the yield and physical properties of these CNTs.

![SEM and TEM photographs of CNT grown on different catalysts from mixed feedstock](image)

The yield and physical properties of the CNTs that were generated from the mixed feedstock followed the same pattern as the CNTs produced from PP, PE and PS.
Figure 19 The (a) yield and (b) physical parameters of CNT by pyrolysis of mixture plastics.
3.3 Discussion

A comparison of the aforesaid CNT yields reveals that for all polymer feedstock T316 seemed to be the most productive catalyst substrate, see Fig 20, and T304 was the least productive. T136L was in between, albeit closer to T316. This variable performance can be partly attributed to the fact that T316 and T316L contain molybdenum (Mo) whereas T304 does not. Molybdenum element will generate molybdenum oxide at the surface upon heat treatment in the air. Molybdenum oxides have been proven to be effective catalysts to generate CNTs by CVD [140, 141]. This was identified as the main reason that T316 and T316L yielded more CNT than T304 at the same experiment conditions. The fact that T316 yield little more CNT than T316L may be due to the fact that T316L has more nickel (Ni) element than T316, as listed in Table 1, Ni element in alloy does not seem to be effective as a catalyst in the synthesis of CNTs from the plastic pyrolyzates. This concept has been proved by experiments in the laboratory where synthesis of CNTs was attempted on a nickel-rich alloy (67% Nickle) mesh and failed. The mass of Ni reduces the mass fractions of other effective elements that can be used as catalysts to synthesis CNT from plastic pyrolyzates. This is offered herein as an apparent reason to explain why less CNT amounts were grown on the T316L than on the T316 substrates.

A comparison of the CNT yields reveals that for the same catalyst substrates, polypropylene was the most productive polymer feedstock, see Fig 20, followed by PE, PS and then PETE. These differences in these yields are caused by the amounts and compositions of the pyrolyzates. PP and PE feedstock contain high amounts of carbon (85.7% each) and (hydrogen 14.3% each). Both pyrolyze effectively (95%) to gas at
800 °C to a variety of light hydrocarbons, including ethylene and propylene, which are effective CNT growth agents [123]. Polystyrene contains more carbon, however, its pyrolyzates contain oils and tars and, thus, less gas than the aforesaid polyolefins, hence its CNT yields are also lower. The yields from PETE feedstock are much lower since it contains even less carbon (62.5%) and its pyrolyzates contain only a limited fraction of gas (less than half of the initial polymer mass [109, 110] and even that gas contains mostly CO and CO₂ [109, 110] and low amounts of light hydrocarbons, which are effective CNT growth agents. The oil fraction contains oxygenated hydrocarbons such as benzoic acid which has been shown to be harmful to the generation of CNTs generating [92, 110].

Figure 20 Comparison of the CNT yield by pyrolysis different plastics
Fig 21 shows the diameters of the generated CNTs. For each polymer feedstock, the diameters are remarkably similar for different similarly-treated catalysts. If feedstock are compared, then the results show that the CNTs from pyrolysis of PP have the minimum diameters (~40 µm), whereas the CNTs from pyrolysis of PETE have the maximum diameters (~80 µm). This shows that the hydrocarbon pyrolyzates have an important influence on the diameters of the generated CNTs. CNT with different diameters have different potential applications. The results of these experiments may be used as a reference for CNT application. For the mixture plastics, the CNTs appear to be mixtures of CNTs with different diameters as the STDEV of these diameters is the highest.

![Diameter of the CNT (nm)](image)

**Figure 21** Comparison of the CNT diameters by pyrolysis of different polymers
For the mixed polymer runs 4 g PP, 4 g PP, 4 g PS and 4 g PETE were used. However, the yield of CNTs from pyrolysis of the combined 12 g of the mixture is less than the yield of CNTs from pyrolysis of 4 g PP or 4 g PE. The reason for this discrepancy is that the polymer pyrolyzates are impacted by those of other plastics. Apparently, the net result was a decrease in CNT yields. One possible reason may be the generation of the problematic benzoic acid from the pyrolysis of PETE, as mentioned earlier. The average diameter of the CNTs that were generated by the mixed polymers is near the average of the CNTs generated form the four polymers. The thickness of the CNTs follows the same trend with the diameter of the CNTs, as it shown in Fig 22.

**Thickness of CNT (nm)**

![Graph showing thickness of CNT (nm) for PE, PP, PS, PETE, and MIX](image)

**Figure 22** Comparison of the CNT thickness by pyrolysis of the different polymers

Fig 23 a shows that the inner structure of the CNT is often segmented. Such a structure is caused by the difference of the carbon diffusion rate between inner and outer layers
of the formed CNTs. Some caps were generated at the inner surfaces because the carbon diffusion rate is slower at the inner space of the CNTs than at their outer space [123, 142-144]. Fig 23 b shows that there are some dark particles inside the CNTs. These dark particles are metal morphologies that are formed by stretching forces. The surface layers of the catalysts melt into a liquid phase at the CNT synthesis working temperature (800 °C) and then they are elongated by the stretching force and finally break into nano-sized particles. The nano particles stay inside of the CNTs and move with the growth of the CNTs [125, 145]. The segmented structure of the CNTs and the metal morphologies cannot be avoided because of the CNT growth mechanism.

Figure 23 TEM images about the quality of the CNT: (a) the inner structure of CNT; (b) dopant in CNT
CONCLUSIONS

• The most effective method for pretreating stainless steels as catalyst substrates for CNT growth is washing by acid (40% HCl) for 10 minutes, heat treating in air for 1 minute and then air-quenching.

• For any given polymer, T316 achieved the highest yield of CNTs. The yield of CNTs on T316L was less than T316, whereas T304 achieved the lowest yield of CNTs.

• T316 and T304 were shown to achieve the growth of ordered forest-like CNTs, whereas the CNTs grown on T316L were typically not ordered.

• The four polymer feedstock generated CNT yields in the following order: PP>PE>PS>PETE.

• The four polymer feedstock generated CNTs with diameters and thicknesses in the following order: PP<PE<PS<PETE.

• The CNT yields from mixed-polymer feedstock were higher than those from PETE and PS, but lower than those of PE and PP.

• The average diameter of the CNTs generated from mixed-polymer feedstock correspond to than average of the diameters of the CNTs generated from the different polymer feedstock.
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