GROWTH OF CARBON NANOTUBES ON CARBON FIBRES
AND THE TENSILE PROPERTIES OF RESULTING CARBON
FIBRE REINFORCED POLYPROPYLENE COMPOSITES

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Abstract
Carbon nanotubes were grown directly on carbon fibres using the chemical
derived deposition technique. The effects of reaction temperature (800-900°C)
and hydrogen gas flowrate (100-300 ml/min) on the morphology of the carbon
nanotube coating were investigated. Carbon nanotubes produced were
characterized using scanning electron microscope and transmission electron
microscope. The resulting fibres were compounded with polypropylene to
produce carbon fibre reinforced polypropylene composites. The tensile
properties of these composites were determined to investigate the effects of the
carbon nanotubes on the overall performance of the composites. The optimum
treatment condition that produced the thickest coating of carbon nanotubes was
obtained at 800°C and 300 ml/min hydrogen gas flowrate. The composite
sample obtained under these conditions demonstrated remarkable enhancement
in tensile properties compared to composites made from as-received carbon
fibres, whereby an increment of up to 52% and 133% was observed for the
tensile strength and modulus respectively.

Keywords: Carbon nanotubes, Carbon fibre, Chemical vapour deposition,
Composite, Tensile Properties.

1. Introduction
It is well known that the fibre/matrix adhesion strength plays an important role on
the mechanical properties of fibre reinforced polymer composites [1]. When load
is applied to composites, it will be distributed and transferred through fibre/matrix
interfaces. A strong bonding promotes a better involvement of more fibres, accordingly increasing the strength of composites. However, carbon fibres usually bond poorly to polymer matrices due to their smoothness and chemical inertness. In order to improve the bonding properties of carbon fibres, various surface treatment approaches can be applied, which can be classified into oxidative and non-oxidative treatments [2].

Oxidative treatments involve gas-phase, liquid-phase and anodic oxidations, whereas the non-oxidative ones include plasma treatments and deposition of more active forms of carbon, such as whiskerization, or grafting of the carbon fibre surface with polymers [3]. Whiskerization treatment increases the strength of the bond by directly growing whiskers on the external surfaces of the fibres so that they bond more securely to the various matrix filler materials to form high-strength composites [4]. Among other material, these whiskers are often either carbon nanotubes (CNTs) or carbon nanofibres (CNFs) which are known for their superior strength [5]. Kowbel et al. [6] reported an improvement of 200%-300% in interlaminar shear strength of whiskerized carbon fibre reinforced epoxy composites. Improvements are attributed to through-thickness reinforcement and increases in interfacial area which increases the surface area of carbon fibres hence providing a larger number of contact points for fibre-matrix bonding [1].

In this work, the whiskerization treatment approach was applied to treat polyacrylonitrile (PAN) based carbon fibres. CNTs were grown directly on carbon fibres using the chemical vapor deposition (CVD) technique. The effects of reaction temperature and carrier gas flowrate on the morphology of the CNT coating were investigated. The CNT coated carbon fibres were then chopped to form short carbon fibres and compounded with polypropylene (PP) to make carbon fibre reinforced polypropylene composites (CFPP).

The rationale for selecting PP as the matrix polymer was because of its wide spread industrial applications in packaging, automotive parts, and it is part of a group of commodity thermoplastics produced in large quantities [7]. Although PP is a relatively softer material, it gained wide spread applications because of its resistance to moisture, corrosion, wear and chemical reactions and extremely low cost [8].

In the present work, the morphology of carbon fibres before and after treatment as well as the composite interface between the reinforcement material (treated and untreated carbon fibre) and polymer matrix (PP) were characterized and the improvement on the tensile properties of the composites were measured.
2. Materials and Methods

2.1. Materials

In order to synthesize CNTs, benzene (Classic Chemical Sdn. Bhd.) was used as the carbon source, ferrocene (Alpha Chemical Sdn. Bhd.) was used as the catalyst precursor, and hydrogen (Malaysian Oxygen Gases Sdn. Bhd.) as the carrier gas. Unsize Polyacrylonitrile (PAN) based carbon fibres (Toho Tenax Co. Ltd.) were used in these experiments, with a density of 1.8 g/cm$^3$ and average diameter of 6 µm and were used as-received. Polypropylene (SM950 grade) (TITAN PETCHEM (M) Sdn. Bhd.) was used as the matrix with melt flow index (MFI) and density of 60 g/10min and 0.9 g/cm$^3$ respectively.

2.2. Carbon fibre surface treatment

In the present work, CNTs were grown on the surface of carbon fibres using a CVD technique in a horizontal quartz tube furnace equipped with appropriate gas feed unit and exhaust gas purging. The experimental set up of the CVD reactor has been described in detail elsewhere [9]. Carbon fibre tows of around 15 cm long were placed in a quartz tube. 1.0 g of ferrocene was placed in a ceramic boat and positioned in the inlet part of the quartz tube. Whiskerization treatment was conducted by introducing hydrogen gas into a container containing benzene and then flowing this reaction gas into the quartz tube where ferrocene and carbon fibres were positioned. In order to investigate the effects of reaction time and carrier gas flowrate on the morphology of the resulting CNTs, four sets of treatment conditions were conducted on carbon fibres at various conditions as outlined in Table 1. A heating rate of 5°C/min was used and the reaction time was fixed for 30 minutes. Argon gas was introduced into the system to create an inert atmosphere during heating and cooling down period.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction temperature (°C)</th>
<th>Hydrogen flow (ml/min)</th>
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<tbody>
<tr>
<td>A1</td>
<td>800</td>
<td>100</td>
</tr>
<tr>
<td>A2</td>
<td>800</td>
<td>300</td>
</tr>
<tr>
<td>B1</td>
<td>900</td>
<td>100</td>
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<tr>
<td>B2</td>
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2.3. Composite processing

CFPP composites containing between 2 and 12 wt.% fibre load were produced by compounding appropriate compositions of carbon fibre (both as-received and treated) and pure PP. Carbon fibres were chopped using a universal cutting mill machine (Pulverisette 19) to a size of 2 mm in length. All compositions were weighted based on weight percentage. Chopped carbon fibres were melt blended with PP in an internal mixer using Thermo Haake PolyDrive with Rheomix R600/610. The mixing process was carried out at 170°C with rotor speed of 55 rpm for 15 minutes. After being compounded, a batch of the blended
composite was compressed into a 15 cm × 15 cm HSINCHU mold with 1 mm thickness and compression molded at 170°C and under the pressure of 150 kg/cm² [2]. The composite samples were then used to determine the tensile strength and tensile modulus.

2.4. Characterization

The morphological characteristics of CNTs grown on carbon fibres and fracture surfaces of tensile specimens were observed using scanning electron microscope (VPSEM, LEO 1455) and transmission electron microscopy (TEM, Phillips HMG 400). Prior to SEM observations, all samples were placed on a carbon double-sided tape and sputter-coated with gold to prevent charge build-up by the electron absorbed by the specimen. The specimens for TEM analysis were prepared by dispersing the samples in ethanol under ultrasonication for 15 minutes at room temperature. A few drops of the suspension were dropped onto a copper micro grid covered with a carbon thin film. The tensile strength and modulus were measured according to the ASTM D638 standard using an Instron Universal Testing Machine Model 4302 under a load of 1 kN and a constant crosshead-speed of 5 mm/min.

3. Results and Discussion

3.1. Growth of CNTs on carbon fibre

The SEM micrograph of carbon fibre is shown in Fig. 1, where it can be seen that the carbon fibre is inherently smooth. Figure 2 shows the post-treated carbon fibres obtained under different reaction conditions. It is clear that CNTs have been successfully grown on the carbon fibres and that different treatment conditions produce different morphologies of the CNT coatings. The CNTs are generally non-aligned with variable lengths as would be expected for reaction temperatures and hydrogen flowrate conditions such as the ones carried out in this work [10]. Note that non-aligned CNTs are more favourable than aligned CNTs for applications such as the nature of this work [10].

![Fig. 1. SEM Micrograph of As-received Carbon Fibre.](image)

The morphology of the CNTs grown on the carbon fibre is directly influenced by the effects of reaction temperature and hydrogen flowrate. The effect of
reaction temperature on the morphology of the CNTs can be obviously seen by comparing Figs. 2(a) and 2(c), whereby the reaction temperature was 800 and 900 °C respectively. It can be seen that at 800°C, long strands of CNTs were produced compared with the relatively shorter strands obtained at 900°C. Furthermore, clumpy microstructures believed to be carbonaceous impurities were present at 900°C. The hydrogen flowrate also had a direct effect on the morphology of the CNTs, as can be seen by comparing Figs. 2(a) and 2(b) as well as comparing with Figs. 2(c) and 2(d). At 800°C, the increase in hydrogen flowrate led to an increase in CNT formation and thus thicker coating, whilst at 900°C it led to the prevalence of carbonaceous impurities.

![Fig. 2. CNTs Grown on Carbon Fibre under Various Reaction Conditions.](image)

(a) A1: 800°C, 100 ml/min hydrogen flow,
(b) A2: 800°C, 300 ml/min hydrogen flow,
(c) B1: 900°C, 100 ml/min hydrogen flow,
(d) B2: 900°C, 300 ml/min hydrogen flow.

The aim of the work is to directly grow CNTs on the surface of the carbon fibres, such that the presence of the CNT network would not only provide a greater surface area for fibre/matrix bonding, but also provide additional strength to the overall composite. In the context of this work, the treatment condition using a reaction temperature of 800°C and hydrogen flowrate of 300 ml/min (Fig. 2(b)) was able to produce a relatively thicker and cleaner CNT coating. The presence of carbonaceous impurities is unfavourable since further purification steps want to be avoided.

The formation of CNTs is highly dependent on the catalyst particle, in this case iron from the decomposition of the ferrocene precursor. It is known that the
catalyst particle has to be of a certain size in order for CNTs to form [11, 12], beyond which the CNT formation is hindered. Furthermore, the surface activity of the iron catalyst particles is also known to be affected by the hydrogen flowrate. Therefore, the explanation for the different morphologies of CNTs obtained under the various treatment conditions can be explained in terms of the catalyst particle size as well as surface activity.

At 900°C and 100 ml/min, the agglomeration rate of the catalyst particles increases leading to the formation of larger and larger catalyst particles. At the same time, carbon from the decomposition of the benzene precursor diffuses into the catalyst particles. However, due to the large size of the catalyst particles, CNTs are unable to form and therefore the diffused carbon forms surface carbide (Fe₃C) along with amorphous carbon and graphite instead. Before long, the catalyst particles becomes deactivated due to carbon poisoning resulting in the formation of clumpy carbonaceous impurities that can be seen in Fig. 2(c). These results are supported by the work of Zhu et al. [13] whereby they reported that the possibility of CNT growth on iron particles is reduced at temperatures higher than 800°C. At this temperature, a higher hydrogen flowrate makes the conditions even worse by increasing the agglomeration rate of the catalyst particles. This explains the prevalence of carbonaceous impurities as can clearly be seen in Fig. 2(d).

It can be deduced that under the current experimental set up, 800°C seems to be an ideal temperature for catalyst particles to deposit onto the carbon fibre and allow the formation of CNTs (Figs. 2(a) and 2(b)). At this temperature, the agglomeration rate of the catalyst particles is relatively minimal such that the particle size remains sufficiently small for CNTs to grow from the carbon diffusion, thus hindering the formation of carbonaceous impurities. Meanwhile, the observed enhancement in amount of CNTs produced when the hydrogen flowrate is increased at this temperature is explained in terms of catalyst surface activity. Hydrogen is known to sustain the activity of iron catalysts by hindering the formation of surface carbide [14]. Therefore, an increase in hydrogen flowrate maintains the metallic surface of the catalyst particle which sustains the CNT growth. This explains the relatively thicker coating of CNTs on the carbon fibre obtained in Fig. 2(b).

Individual CNTs were also characterized using TEM micrographs as shown in Fig. 3. These images confirm that under the current experimental set-up, multiwalled CNTs were obtained. The diameter of the CNTs was uniformly 20–40 nm with an average value of 30 nm.
3.2. Tensile properties of CFPP composites

To demonstrate the effects of the whiskerization treatments on the tensile properties of resulting CFPP composites, tensile tests were carried out on composites made from samples A1, A2, B1 and B2. The results of the tensile strength and tensile modulus of the composites are shown in Figs. 4(a) and (b) respectively. The properties of the CFPP composite made from as-received carbon fibres are also shown for comparison.

It is evident that the presence of CNTs on the surface of the carbon fibres has a direct impact on the tensile properties of the resulting CFPP composite. Unlike the composite made from as-received carbon fibres, the tensile properties of treated carbon fibre composites generally increased for all treatment conditions. The range of increment in tensile strength and modulus for each composite type measured at 2 – 12wt% fibre content are tabulated in Table 2.

Table 2. Composite Type and Range of Increment (%).

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<tr>
<th>Composite type</th>
<th>Treatment Conditions</th>
<th>Range of Increment (%)</th>
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<tr>
<td></td>
<td>Reaction temperature, (°C)</td>
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Further investigation in terms of CNT morphology modulation and fibre/matrix chemical interaction would be required to better explain the tensile behaviour of each sample as well as the anomalous effects of fiber content loading. However, as far as the current work is concerned, as expected the highest increment in tensile properties was achieved by sample A2, especially in terms of its tensile modulus. The tensile strength and modulus for sample A2 was approximately 27 and 1068 MPa respectively, which translates to an increment of 57 and 133% respectively.

The improvements in tensile properties are attributed to the relatively thick CNT coatings grown on the surface of the carbon fibres with good coverage and very minimal carbonaceous impurities. CNTs are known to have superior mechanical strengths. Therefore, the randomly oriented network of CNTs grown on the surface of carbon fibres not only enhances the fibre/matrix interfacial bonding due to the significant increase in surface area but also shares the stress transfer along with the carbon fibres. It has also been said that within the matrix, the CNTs help fibre anchorage in a manner similar to what roots can do to a tree [15]. The CNT morphology modulation, and chemical interaction with the matrix would also play a role but is currently outside the scope of the current work. The presence of CNTs at the fiber/matrix interface are expected to enhance the matrix bonding when they are well attached to the fiber surface and resin has sufficiently penetrated into the CNT arrays [10]. Further studies are needed to understand the interaction and bonding mechanism at the CNT/matrix interface and thus the fracture mechanism of composites of this nature.
4. Conclusions

CNTs were successfully grown on the surface of carbon fibres using the chemical vapour deposition technique. Reaction temperature and hydrogen flowrate had a direct influence on the morphology of the CNTs. A thick coating of CNTs with minimal carbonaceous impurities were obtained at 800°C and hydrogen flowrate of 300 ml/min. CFPP composites made from CNT coated carbon fibres saw an improvement of up to 57 and 133% in terms of tensile strength and modulus respectively. It can be concluded that the significant improvement in the tensile properties of CFPP composites is attributed not only to the enhanced fibre/matrix bonding afforded by the CNTs but also the ability of the CNTs to participate in sharing the stress transfer along with the carbon fibres.
References