GRAFTING CARBON NANOTUBES ON CARBON FIBERS WITHOUT LOSS IN CARBON FIBER STRENGTH, USING THE EQUIMOLAR C_2H_2-CO_2 REACTION

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Abstract
Carbon nanotubes (CNTs) are grown directly on the surface of PAN-based carbon fibers by means of catalytic chemical vapor deposition (CVD) technique. To solve the problem of carbon fiber degradation during the CNT grafting process, CNTs are grown using the equimolar C_2H_2-CO_2 reaction. This reaction enables the growth of CNTs at much lower temperatures, down to 500°C. Single-fiber tests are carried out to assess the influence of the grafting process on the carbon fiber mechanical properties. Scanning electron microscopy images are taken to study the CNTs and their distribution. Single-fiber tests have shown that CNTs can be grown on carbon fibers without loss in carbon fiber strength.

1 Introduction
Carbon nanotubes (CNTs) have attracted a lot attention the last two decades because of their exceptional mechanical properties, combined with a low density and high aspect ratio. One of the most promising applications is the use of CNTs as nano-reinforcements in polymer composites, more specifically in carbon fiber reinforced polymers (CFRPs). Since CNTs cannot compete with carbon fibers as *primary* reinforcements in polymer matrix, CNTs are often used as *additional* reinforcements in combination with carbon fibers. There are several ways to introduce CNTs in CFRPs, which have been reported and reviewed extensively in the literature [1,2]. A very interesting approach is the direct growth of CNTs on carbon fibers [3-8]. This approach has the potential to significantly reinforce the fiber/matrix interface and to hence hinder fiber/matrix debonding in the early stages of damage development.

However, a serious drawback of this approach is degradation of the carbon fibers during the CNT grafting process. The metallic catalytic particles (Fe, Co and/or Ni) can interact with the carbon fiber, causing damages to the fiber surface and resulting in degradation of tensile strength and strain-to-failure.

In this study, CNT are grown on carbon fibers using an alternative chemical vapor deposition (CVD) route, namely the equimolar C_2H_2-CO_2 reaction [9-12]. This reaction is based on oxidative dehydrogenation reaction of C_2H_2 and CO_2. It allows growing CNTs at significantly

lower growth temperatures. Compared to a traditional CVD process, which relies on thermal decomposition of hydrocarbon, the growth temperature can be lowered from 700-800°C down to 500°C. Single-fiber test indicate no loss in mechanical properties of the CNT-grafted carbon fibers produced at 500°C.

2 Materials and testing methods

2.1 Raw materials

The carbon fibers used in this study are AS4C PAN-based carbon fibers, arranged in bundles of 6000 fibers, taken from a woven twill 2/2 fabric (G0986 Injectex, Hexcel). Prior to catalyst deposition and CNT growth, the fiber sizing is removed by heating the fibers in an inert Ar atmosphere at 450°C for 15 minutes. This procedure is selected based on TGA measurements [11].

The catalyst preparation involves bi-metallic salt solutions prepared by dissolving Fe(III) nitrate nonahydrate and Ni(III) nitrate hexahydrate in ethanol with a Fe/Ni ratio fixed to 2:1 in order to reach the composition of the most active catalyst in the Fe-Ni system, namely Fe_2Ni [12]. Carbon fibre bundles (not individually separated fibres) are impregnated with the catalyst solution by dipping and immersing them for about 16 hours. Subsequently, the bundles are removed from the solution, excess solution is wiped off, and the bundles are dried in an oven for one hour at 80°C.

2.2 CVD process for CNT growth

The grafting of CNTs is performed in a horizontal quartz tube furnace. To be precise, carbon fibre bundles impregnated with catalyst are placed into the quartz tube for 10 minutes, while Ar is introduced with a flow of 45 l/h. Two different recipes are used: The first recipe involves traditional thermal decomposition of hydrocarbon, this is referred to as "traditional" CVD process in the text. Carbon fibres are exposed to a gas mixture of C_2H_4, H_2 and Ar for 30 minutes (0.2 l/min C_2H_4 : 0.2 l/min H_2 : 2 l/min Ar). Alternatively, oxidative dehydrogenation of C_2H_2 and CO_2 was applied as described previously [9, 10]. A mixture of C_2H_2 and CO_2 with a 1:1 stoichiometry (1 l/h) is added to Ar. After exposure to reactive gases, bundles remain in Ar flow for 10 min and finally are moved out from the heated zone and cooled down to room temperature.

2.3 Characterization techniques

CNT-grafted carbon fibers are imaged with Philips XL30 FEG scanning electron microscope (SEM) operating at 10 kV. Single-fiber tests are performed according to the ASTM D3379 standard with a gauge length of 25 mm and a test speed of 500 µm/min. A 18 N load cell with a resolution of 1 µN and a crosshead with a displacement resolution of 1 nm are used to record force and displacement, which are then converted to stress and strain. Before each test, the exact gauge length is measured automatically (Q800, TA Instruments). Strength is taken as the maximum stress whereas stiffness is derived from the tangent slope of the stress-strain curve between 0.1 and 0.3% strain.

3 Results and discussion

3.1 CNT growth

CNTs are grown on carbon fibers, using the "traditional" CVD process, which is based on thermal decomposition of C_2H_4 and therefore requires high temperatures (i.e. 700-800°C). Figure 1 shows SEM images of carbon fibers after the CNT grafting process performed at

different temperatures. At 700°C, a homogeneous CNT coverage is achieved, whereas at 650°C only very few CNTs can be found. At temperatures below 650°C, no CNTs were grown. Very thick carbon structures can be observed at 750°C, mostly between the fibers. It is assumed that catalytic particles undergo Ostwald ripening at this high temperature and migrate in-between the fibers, leading to thick carbon structures. Based on SEM investigation, it can be concluded that with the traditional CVD process, CNTs can only be grown on carbon fibers in the temperature range of 650°C to 750°C, with an optimal growth temperature of 700°C.

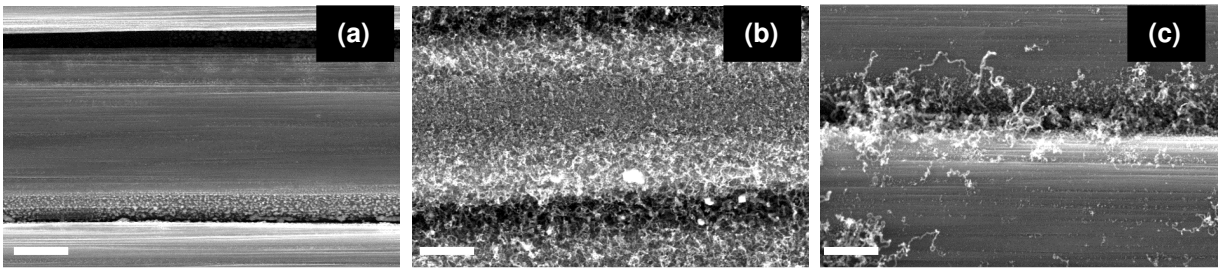

Figure 1. SEM images of CNT-grafted carbon fibers produced with the traditional CVD process at (a) 650°C, (b) 700°C and (c) 750°C. Scale bars equal 2 µm.

After removing CNTs from the carbon fibers, damage is clearly visible at the fiber surface (see Figure 2b). Compared to the smooth and damage-free surface of the as-received fibers (see Figure 2a), the surface of CNT-grafted carbon fibers produced at 700°C is attacked by the catalytic particles, leading a rough surface caused by pitting. These pits are responsible for a significant decrease in fiber strength and strain-to-failure. This will be discussed in more detail in the next section.

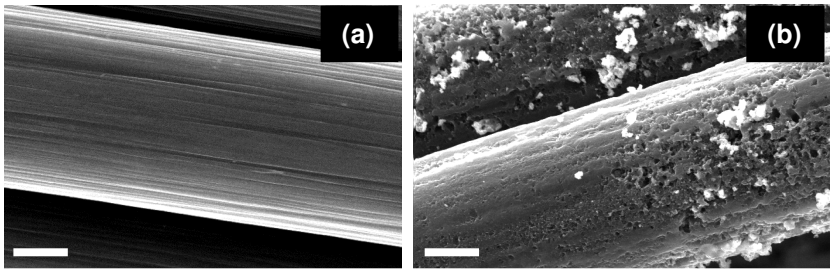

Figure 2. SEM image of (a) as-received carbon fiber and (b) CNT-grafted carbon fiber produced at 700°C by the traditional CVD process after removing the CNTs. Scale bars equal 2 µm.

More detailed investigation revealed that the high temperature is the main driving force behind this pitting phenomena [11]. A lower growth temperature (i.e. 500-600°C) could prevent this and hence maintain the fiber strength after the grafting process. However, the traditional CVD process is limited to the thermal decomposition at high temperature (>650°C). It has recently been reported that CNTs can be grown below 400°C using the equimolar C_2H_2-CO_2 reaction. This reaction is based on the oxidative hydrogenation reaction of C_2H_2 with CO_2 that yields carbon atoms in order to form CNTs via chemical reaction. As highlighted by Magrez et al. [9], the activity and the lifetime of the catalysts are enhanced to such an extent that high yield of CNTs can be grown at significantly lowered growth temperatures. We applied this equimolar C_2H_2-CO_2 reaction to grow CNTs on carbon fibers. The SEM images are given in Figure 3. At 750°C, thick carbon structures are produced between the fibers, similar to the ones grown with the traditional CVD process. At 600°C, a nice homogeneous CNT coverage on the fibers is achieved. Also at 500°C, CNT were

observed, although they are much shorter. The growth efficiency at this temperature is further improved by applying a H_2 pre-treatment to the catalyst particles. Note that with the traditional CVD process, the temperature range for growing CNTs was limited to >650°C.

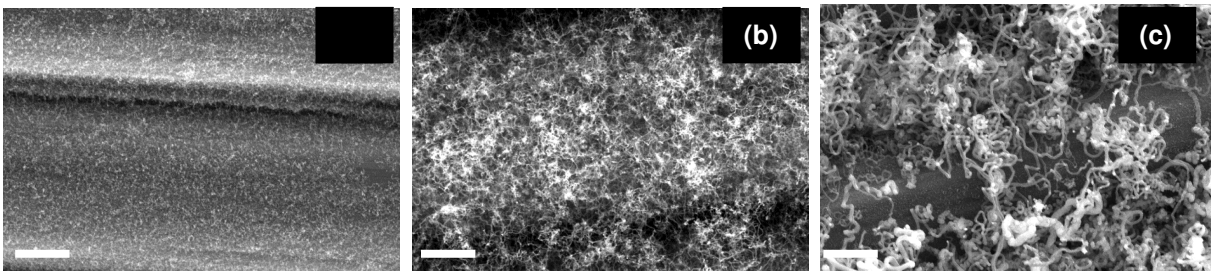

Figure 3. SEM images of CNT-grafted carbon fibers produced with the equimolar C_2H_2-CO_2 reaction at (a) 500°C, (b) 600°C and (c) 750°C. Scale bar equals 2 µm.

3.2 Mechanical properties of carbon fibers

In the previous section, it has been demonstrated that CNTs can be grown at 500°C with the equimolar C_2H_2-CO_2 reaction. In this section, the results of single-fiber tests on CNT-grafted carbon fibers produced with both the traditional CVD process and equimolar C_2H_2-CO_2 reaction are reported. The mechanical properties of interest are Young's modulus, tensile strength and strain-to-failure.

In Figure 4, a typical stress-strain curve for an as-received carbon fiber is given, as well as for a CNT-grafted carbon fiber produced with the traditional CVD process at 700°C. It can be noted that there is no effect of the grafting process on the Young's modulus, while both the tensile strength and strain-to-failure show a decrease of almost 50%. This significant decrease can be explained by the fact that the grafting process introduces damage to the carbon fiber surface, under the form of small pits (as been shown in Figure 3b). These pits act as a defect and cause early failure of the carbon fiber, resulting in a decreased tensile strength and strain-to-failure. The carbon fiber core is not affected by the surface, which is reflected in a constant Young's modulus. This corresponds to observations reported in literature [3-8].

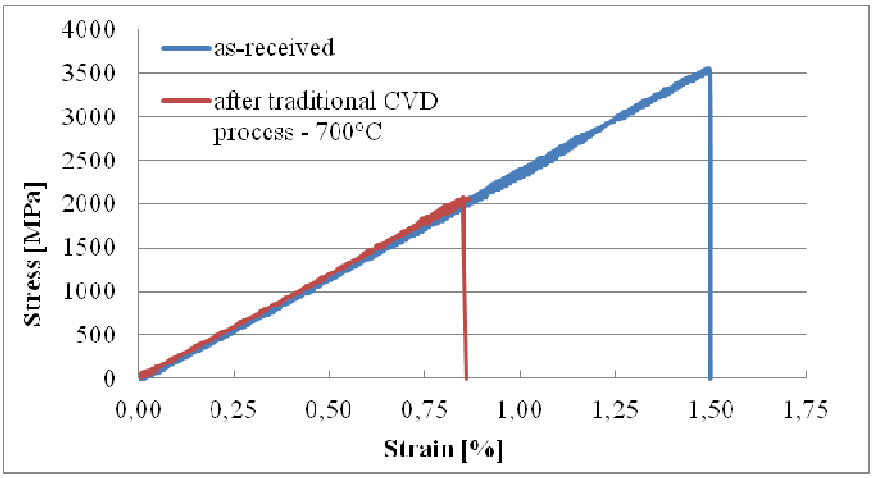

Figure 4. Typical stress-strain curves of as-received carbon fibers and CNT-grafted carbon fibers produced with the traditional CVD process at 700°C

In Figure 5, the tensile strength of CNT-grafted carbon fibers is given for different growth temperatures. The values of the as-received carbon fiber are also included for comparison. For

the equimolar growth, values for the growth with a reducing H_2 pre-treatment are also included.

The carbon fiber tensile strength (see Figure 5) shows a significant influence on the growth temperature for both the traditional CVD process and equimolar C_2H_2-CO_2 reaction. At a growth temperature of 700°C, the tensile strength is reduced by almost 50% compared the as-received carbon fiber. This decrease in tensile strength is less pronounced at lower growth temperature (-18% at 650°C) and is even absent at growth temperatures of 600°C and lower. However, as discussed in the previous section, there are no CNTs grown at these low temperatures with the traditional CVD process. With the equimolar C_2H_2-CO_2 reaction, on the other hand, CNTs could be grown at temperature down to 500°C.

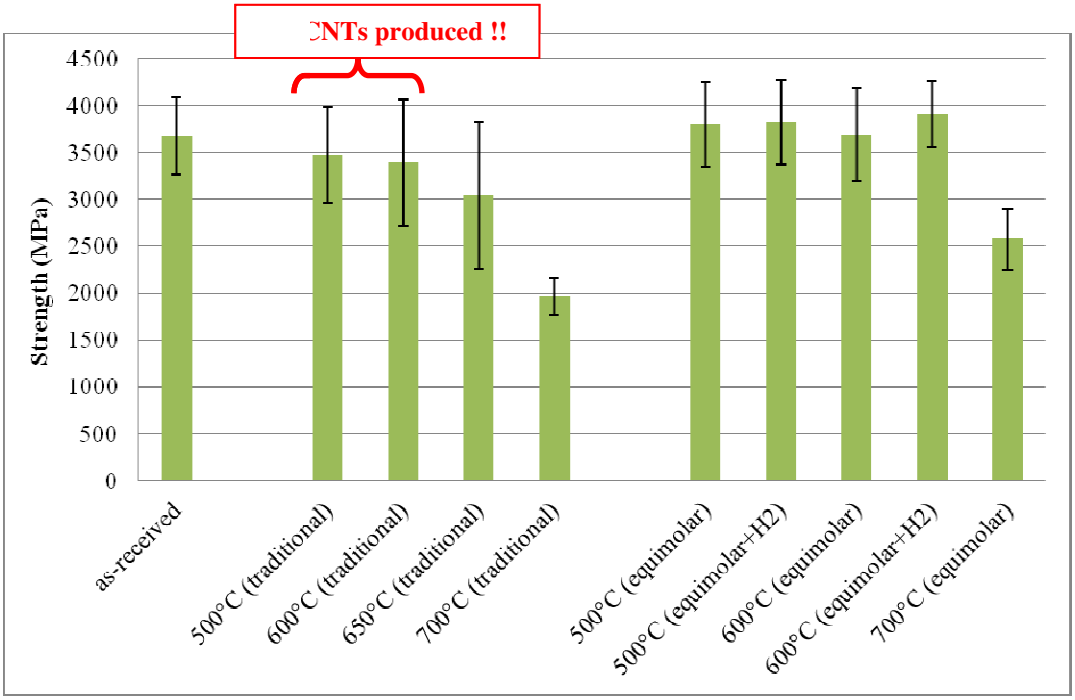

Figure 5. Tensile strength of CNT-grafted carbon fibers produced with the traditional CVD process and with the equimolar C_2H_2-CO_2 reaction at different temperatures.Carbon fibers before the CVD process are included as 'as-received'.

The values for the Young's modulus are not given, since these values do not change after the grafting process (as explained above). Concerning the strain-to-failure, similar results are obtained as for the tensile strength. This is a direct consequence of the linear stress-strain curve of the carbon fibers. For the strain-to-failure, the same conclusion can hence be drawn as for the fiber tensile strength.

4 Conclusion

In this study, we have demonstrated that grafting CNTs on carbon fiber is possible without degradation in carbon fiber strength and strain-to-failure. The key-to-success is the use of a lower growth temperature, which is enabled by the equimolar C_2H_2-CO_2 reaction. Traditional CVD processes are only capable of growing a high density of CNTs at temperatures between 650 and 750°C. The equimolar C_2H_2-CO_2 reaction, on the other hand, allows us to grow CNTs on carbon fibers at 500°C. As a result of this low growth temperature, catalyst particles do not interact with the carbon fiber and hence do not cause damage. Whereas the carbon

fibers suffer from a 40-50% reduction in tensile strength at 700°C, there is no reduction at all when CNT are grown at 500 or 600°C. These results can be an important step towards more damage resistant CFRPs without sacrificing other mechanical properties.

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