Manufacturing of a Continuous Carbon Nanotube Rollstock

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ABSTRACT

Continous manufacturing of multiwall carbon nanotubes from forest to nonwoven rollstock has been demonstrated. The processes consist of liquid catalyst generation, nanotube synthesis and nonwoven formation. Each of the unit operation has corresponding patent applications. The quality of nanotubes generated under the new continuous schema is similar to the traditional batch processes, i.e. electron beam catalyst depositon and batch chemical vapor deposition. In addition to the expected cost reduction and enhanced throughput, the new schema offers flexibility to tailor-make properties from vertically aligned nanotubes on rollstock to low or high resistance nonwovens. The rollstocks are seamless and are compatible with existing roll-to-roll prepreg operations. Examples of application evaluations from aerospace to industrial durables will be presented.

Keywords: high volume carbon nanotube manufacturing, forest CNT, vertical aligned CNT, nonwovens

1 INTRODUCTION

Over a decade ago, the National Nanotechnology Initiative was authorized by President Clinton at Caltech in 2000. A good deal of science and fundamentals were ascertained in this period at the nanoscale. Practitioners and investors have benefited with scientific insight. In recent years, nanomaterials are being described in manufacturing or macro perspective instead of scientific curosity . In this presentation, General Nano will highlight our modular, continuous, and flexible processes to deliver multi-millimeter, high purity, vertically aligned carbon nanotubes (CNT) and/or handleable nonwoven rollstock (seamless, roll-to-roll) at high volume throughput to afford systems level evaluation and applications.

2 DIFFERENTIATED CNT

In the mid 2000's, significant advances were reported in the synthesis of CNTs. Major methods of synthesis were described (Rafique & Iqbal, 2011), e.g., arc discharge, laser ablation, floating catalyst, and chemical vapor deposition. Today, commercial production of CNTs is focused in two camps – mass throughput and ultra-long nanotubes. The high throughput process is generally achieved via floating catalyst (Morançais, Caussat, & Kihn, 2006), where the catalyst is in gas phase. The average lengths of the nanotubes are in the order of 10 microns. Its first pass purity ~80% nanotubes. The ultra-long nanotubes are usually grown on substrates and is well documented (Zhang, Zhang, & Wei, 2014). In 2007, the NSF reported the longest nanotubes produced at 2 cm (Schulz & Shanov, 2007) with high purity (~99.5% CNT), see Figure 1. The Schulz-Shanov process is a proprietary catalyst on silicon. Recently, General Nano has converted the Schulz-Shanov process to a liquid coated catalyst, roll-to-roll process. Millimeter-height nanotubes are continuously grown on this catalytic rollstock with comparable purity and density. The long lengths, high aspect ratio and purity of nanotubes are requisite for downstream processes described below.

Figure 1. 2cm CNT

3 MANUFACTURING PROCESSES

3.1 Manufacturing Strategy Differentiation

Producing large volume of long length and high purity nanotubes is a daunting technical challenge. One approach to high volume is to serialize the process. This strategy makes sense when fundamentals are mostly known. The product properties are specific. And, strong financial and human resources are prerequisites for execution. Another approach is to decouple the production into discrete unit operations, where each risk can be isolated and conducive to concurrent engineering. The advantages are flexible and agile product development and customizable properties to specific customers or market segments. Products from each operation can be potential revenue streams. And, capital expenditure is miminized via strategic outsourcing if patent protection is in place for each unit operation. We will describe the latter approach for production scale-up.

3.2 Liquid Catalyst (LC)

Historically, substrate-grown nanotubes require specific catalyst to be deposited on a silicon wafer under high vacuum (Morançais, Caussat, & Kihn, 2006). This batch process, typically electron beam deposition, is limited in throughput (lb/hr) and surface area. In addition, frequent maintenance of vacuum pump is necessary. The advantage is high precision, layer thickness control (O(10 nm)).

Moving from an industry standard to a liquid coating process, with constraints of layer precision and "high" line speed, requires innovation in catalyst and process engineering. The patent pending process at General Nano is based on liquid coating on common grade stainless steel (Figure 2). Based on X-Ray Photoeletron Spectroscopy (XPS), both the electron beam (EB) and liquid catalyst have comparable coating depth profiles. The mass density of LC was demonstrated to be higher than EB. Overall, the mass productivity of LC was shown to be >50x of the EB procoess.

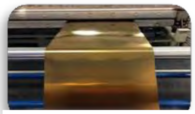

Figure 2. Roll of Liquid Catalyst.

3.3 Chemical Vapor Deposition (CVD)

CVD on substrate is the preferred synthesis method at General Nano for high purity and tall nanotube forest (Figure 3). The key process control variables for forest density and heights are typical chemical reactor variables: gas species and concentration, gas temperature and residence time. To quantify growth kinetics, we conducted computational fluid dynamics to visualize streamlines, turbulence intensity, and temperature distribution along the substrate. This was the basis of new reactor designs for roll-to-roll at atmospheric operations. Recently, a proof of concept was demonstrated at a scaleable rate of 1 kg/day.

Figure 3. CNT Forest on Stainless Steel Belt

3.4 Nonwoven Production

From continuous catalyst deposition to continuous CNT sysnthesis, the next operation is to produce a continuous rollstock to be compatible with downstream operations such as prepreg integration. This patent pending process leverages existing technology, albeit significantly modified, for nonwoven formation and easy release onto prepreg (Figure 4). Key barriers overcame were the degree of dispersion and its stability, formation uniformity, consolidation, and roll formation. The process window is sufficiently robust that hundreds of feet of rollstock can be produced per shift.

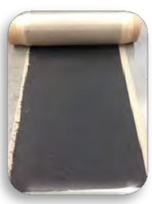

Figure 4. Rollstock of Nonwovens.

This process was selected for its flexibility to produce a wide range of stock keeping units (SKUs). In Figure 5, we demonstrated that sheet resistance can be designed and controlled by 2 orders of magnitude. This provides a multitude of applications that we'll report below.

Figure 5. Capability of Broad Range of Sheet Resistance.

4 APPLICATIONS

4.1 Deicing

Utilizing the nonwoven process, the ability to design sheet resistance is demonstrated in Figure 6. Dialing in the material composition of the nonwovens, a sheet resistance of 40 Ω/□ was made. The temperature profile and its uniformity afford a unique lightweight heating element design for unmanned air vehicles, where weight reduction is a key value proposition.

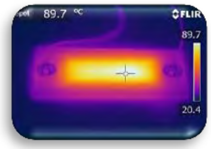

Figure 6. Temperature Uniformity in an Deicing Application

In another application, vertically aligned nanotubes (VACNT) were grown on a proprietary substrate for stray light absorption. From the CVD reactor, the heights and density of nanotubes were optimized per customer specification for electro-optical instruments.

Figure 7. VACNT for Sensors

Because VACNT can be grown on a continuous belt, z-direction prepreg reinforcement is a possibility to enhance mechanical strength of composites. Validation is underway.

5 SUMMARY

From growing long CNTs on a swatch of silicon, continuous processes to manufacture rollstock with tunable form factors and properties were demosntrated. Several applications were highlighted to support commercialization of this new material category.

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