Scalable Manufacturing of High-Nanotube-Content Nanocomposite Fabrics

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ABSTRACT

Integration of nanotubes in the form of fabrics or other preformed assemblies (sheets, films, fibers, etc.) simplifies their handling and allows for higher nanotube content, which is needed to better leverage their amazing properties and achieve advanced composite materials with improved performance. Here we highlight the development of a novel carbon nanotube (CNT) – thermoplastic polyurethane (TPU) fabric material with high CNT content (from ~10 wt% to ~60 wt%). The properties of the fabric are tailorable based on the composition (ratio of nanotubes:polymer) and the choice of the nanotube and TPU materials. Fabric production by filtration was scaled to 30 cm square sheets and currently, as shown here for the first time, to a continuous method using an aerosol spray. The new method will enable pilot-scale manufacturing – an essential step towards commercialization of the material – as well as direct deposition onto other substrates for production of high-nanomaterial content composites.

Keywords: nanotubes, thermoplastic polyurethane, fabric, manufacturing, scale-up

1 INTRODUCTION

Carbon nanotubes (CNTs) have long been considered promising for development of advanced composite materials, due to their unsurpassed properties along with low density, and they are now appearing in an increasing number of composites applications from sporting goods to aerospace [1,2]. Most commonly, CNTs are integrated via dispersion into a matrix. The dispersion approach is effective but is limited to low nanotube content (on the order of < 0.1 to a few percent by weight. In contrast, the approach of using a preformed, macroscopic assembly of nanotubes (a yarn, film or fabric) allows for higher local content of nanotubes (up to > 60 wt%), which is useful to better leverage their functional properties and is also advantageous in terms of nanomaterials safety and for integration as an interlaminar or surface layer.

The earliest and most-common fabric-like materials have been CNT papers called buckypapers [3], which are often produced by filtration. Although buckypaper is effective as a pre-form for composites fabrication; such paper-like sheets often have poor mechanical properties, in some cases three to four orders of magnitude lower tensile properties than the CNTs (*e.g.*, a few hundred MPa in modulus and only a few MPa in strength) [4]. CNT yarns and sheets formed from long, aligned CNTs have yielded the highest properties for macroscale CNT materials and nanocomposites. A few such materials are commercialized [5-7]; however, this type of CNT material is relatively high cost and not yet broadly available.

Currently, we are developing scalable methods for production of nonwoven CNT-thermoplastic polyurethane (TPU) fabrics made from broadly available, low-cost, industrial-grade nanotube powders based on a dispersion and filtration method [8,9]. In that approach, use of a solvent/non-solvent system results in controlled adsorption of TPU on the nanotube surface leading to recovery of a nonwoven fabric of TPU-coated nanotubes following filtration. The method provides for tailoring of the composition (nanotube:polymer ratio) and the properties of the resulting nanocomposite fabrics, and was scaled directly to produce sheets up to 30 cm x 30 cm in size. Most recently, the approach has been adapted to recover the sheets by aerosol spraying, demonstrating proof-of-concept for continuous manufacturing (roll-to-roll) while achieving similar and improved properties.

The prepreg-like nanocomposite fabrics can be handled and employed analogously to other fabric and prepreg materials, and layered, laminated or infused to produce thick nanocomposites, or integrated with conventional fabrics and composites. Lab demonstrations show high potential for a range of multifunctional applications (*e.g.*, heating, electromagnetic shielding, flame resistance).

2 CNT-TPU FABRICS: LAB SCALE

2.1 Solvent-Nonsolvent Filtration Method

Fabrication of CNT-TPU nanocomposite fabrics by filtration is illustrated in Figure 1. The fabrics discussed here are fabricated primarily using Nanocyl NC7000 Industrial-grade MWCNTs (Nanocyl SA), or using Tuball (OCSiAl) for the the case with SWCNTs, and a thermoplastic ester-based TPU (UAF 472 from Adhesive Films Inc). Other TPU materials and a range of CNT samples with varying synthesis method, diameter and length have been employed in lab scale tests with emphasis on using cost-efficient, industrial grade and scale materials.

In contrast to typical filtration methods for buckypaper, the approach employs two solvents (a solvent dissolving the TPU and a TPU non-solvent in which the CNTs are first dispersed) that, when combined, yield a slurry from which a non-woven fabric of TPU-coated CNTs (Figure 1) can be quickly recovered by vacuum filtration [8]. We previously demonstrated, using adsorption isotherms, that the quantity of TPU adsorbed on the CNT surface depends on its initial concentration in solution, which provides a convenient approach to tailor the composition (e.g., from ~10 to > 60 wt.% CNTs) and the properties of the sheets [8]. While the presence of the TPU component may be a limitation in certain application cases, this novel nanocomposite fabric offers a range of advantages in comparison to other nanotube-based sheets, including:

- Convenient nanomaterials handling (use in a robust fabric form)
- Fast filtration (much faster than filtering with dissolved polymer)
- Compositional control (controlled TPU adsorption)
- Tailorable properties, including high failure strain
- High nanotube content (~10 to ~60wt%)
- Lightweight (~ 0.7 to 1.4 g/cm^3)
- Cost-effective (uses industrial-grade CNT powders)

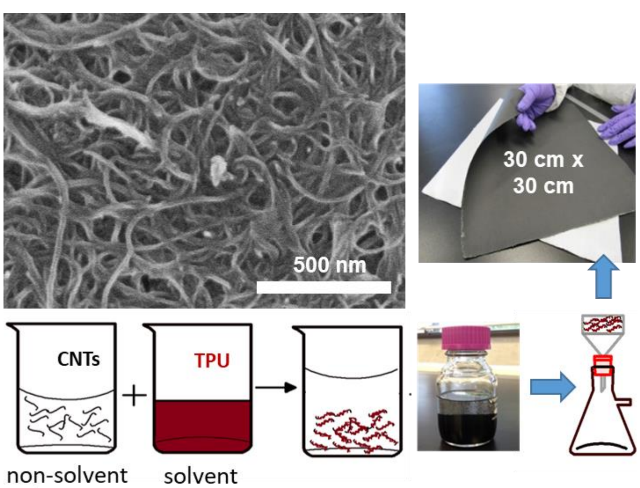

Figure 1: Preparation of CNT-TPU nanocomposite fabrics by a 2-solvent, vacuum filtration method.

2.2 Tailorable Properties

Tensile properties and electrical conductivity of CNT-TPU sheets produced using NC7000 MWCNTs (dispersed in methanol) and UAF 472 TPU (dissolved in acetone) are shown in Figure 2 [8]. There is an optimum in properties around the 35:65 CNT:TPU weight ratio, which appears to give the highest tensile strength and stiffness while also having relatively high failure strain and electrical conductivity. Notably, the electrical conductivity for this composition is similar to a buckypaper comparison sample (nominally 100% MWCNTs) despite containing more TPU than CNTs by weight, which we attribute to a thin TPU coating also improving exfoliation of the CNTs and their packing in the final fabric.

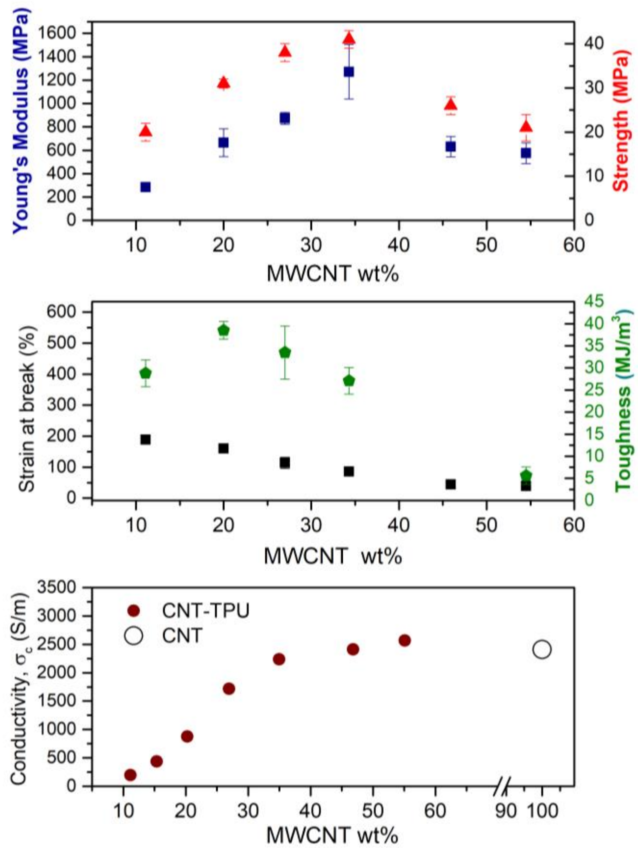

Figure 2: Example properties of MWCNT-TPU sheets. Re-plotted from Martinez-Rubi et al. [8].

Properties of the CNT-TPU fabrics can also be adjusted for higher stiffness, strength, strain, toughness, conductivity, etc., through selection of both the type of TPU and the type of CNTs, as well as using alternative nanoparticles like boron nitride nanotubes [10], graphene nanoplatelets, *etc*. Table 1 reports the tensile and electrical properties at the optimal composition for fabrics with NC7000 MWCNTs and Tuball SWCNTs. Notably, the strength, stiffness and conductivity are higher in the case with SWCNTs and the properties achieved with relatively low-cost industrial CNTs are becoming more comparable to that to high-performance CNT materials than to lower performance CNT papers.

Material	CNT wt%	Density (g/cm^3)	Elastic Modulus (GPa)	Strength (MPa)	Electrical conductivity (S/m)
MWCNT-TPU*	35	0.94	1.2	40	2,500
SWCNT-TPU*	43	0.9	3.2	150	11,000
MWCNT* buckypaper	100	0.3	0.2	2	2,500
SWCNT* buckypaper	100	0.45	1.9	40	20,000
Miralon† CNT sheet	100	0.65	-	30-130	39,000

Table 1: Example comparison of CNT-TPU sheets to buckpapers prepared with the same CNTs and to high-performance, commercial CNT sheets. *Present work using UAF 472 TPU and NC7000 MWCNTs or Tuball SWCNTs. †Manufacturer data (Huntsman [5]): density: 0.65 g/cm^3; specific strength: 50-200 MPa/(g cm^{-3}); specific conductivity: 600 S cm^2/g).

2.3 Application cases

Figure 3 illustrates several application cases employing CNT-TPU nanocomposite fabric as a surface or interlaminar layer including for sensing, heating, electromagnetic shielding, flame resistance, hydrophobicity and energy absorption. The electrical properties, even with the modest conductivity MWCNT-TPU fabrics (2500-3,000 S/m), can offer effective electromagnetic shielding as can be seen from measurements of the S-parameters (S_{12}) as well as provide for electrical heating and strain-sensing. In the cases shown here, the TPU-component also tends to be advantageous and can be selected to improve adhesion.

3 TOWARDS ROLL-TO-ROLL MANUFACTURING

The 30 cm sheets produced by filtration have enabled a series of lab-scale demonstrations at the National Research Council (NRC) Canada; however, larger-scale and continuous production presents a critical challenge to support pilot-scale applications and industry engagement. To this end, Integran Technologies Inc has demonstrated a proof-of-concept for continuous manufacturing. The process to continuously produce CNT-TPU fabrics (Figure 4) involves four stages:

(i) CNT-TPU slurry production;
(ii) slurry deposition onto a continuous conveyor belt via pressurized spray guns;
(iii) solvent evaporation to form solid fabrics;
(iv) hot-roll-pressing to improve fabric density and properties.

The proof of feasibility for deposition by pressurized spray guns onto peel-ply was confirmed when sprayed slurries dried and formed continuous, homogeneous CNT-TPU fabrics that were easily separated from the peel-ply (Figure 5). Fabric samples were produced with thicknesses from < 50µm to > 250µm, and typically as 20 cm x 20 cm sheets but in some cases > 30 cm x 50 cm.

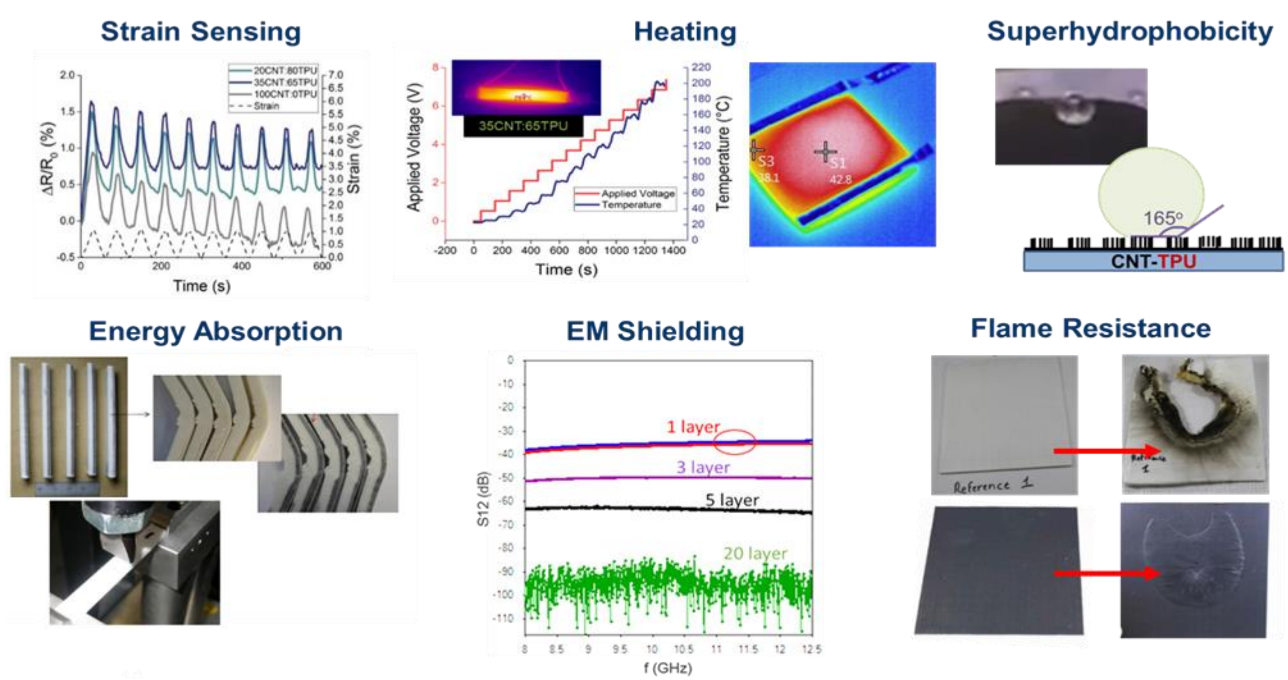

Figure 3: Application-related performance examples based on electrical properties (sensing/heating/shielding), thermal properties (flame resistance), energy absorption and patterned, hydrophobic surfaces.

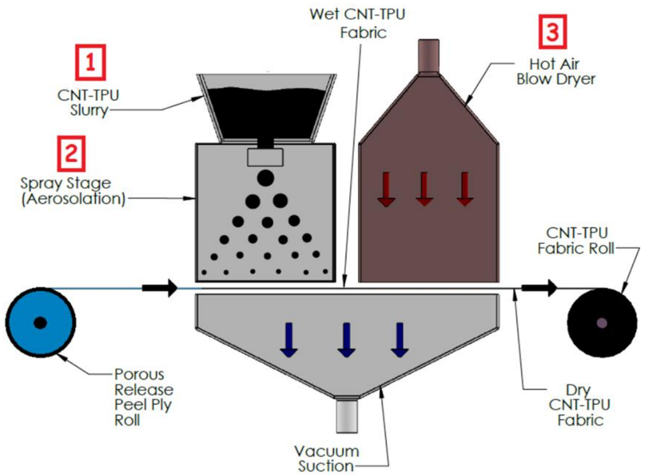

Figure 4: Schematic illustration for roll-to-roll, continuous manufacturing of CNT-TPU sheets. Stage 4 (hot-roll-pressing) is optional and not shown in the illustration.

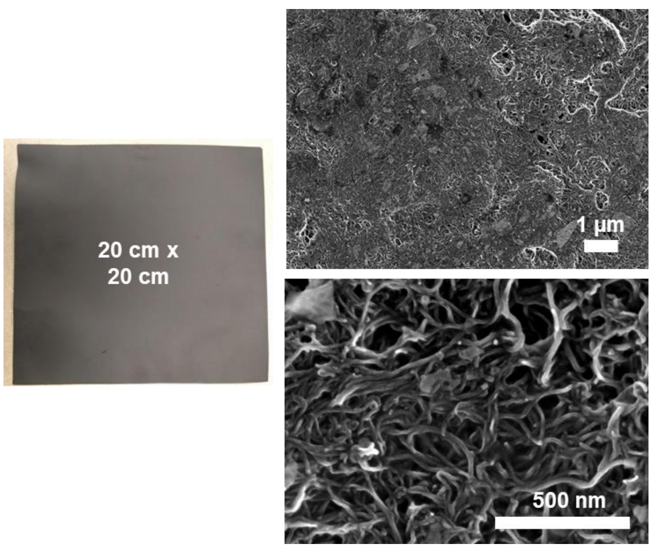

Figure 5: CNT-TPU sheet produced by the spray method.

Using the same MWCNTs and TPU as shown in the lab-scale filtration sheets, a sprayed and hot-roll-pressed fabric sample of 34 wt% MWCNTs (comparable to the optimal composition observed in the lab-scale process) was measured to have: thickness of 116 µm, density of 1.41 g/cm^3, conductivity of 3020 S/m, elastic modulus of 1250 MPa, UTS of 78 MPa, and failure strain of 83%, which meets or exceeds the properties of similar filtration-produced fabrics.

4 CONCLUSIONS

Nanotube-based fabrics are emerging materials within the CNT commercial market and can be expected to find broad applications. They enable high nanotube content to better leverage properties, and simplify handling for increased nanomaterials safety and ease-of-integration. The nonwoven CNT-TPU fabric described here:

(i) Demonstrates a novel approach using cost effective, industrial-grade CNTs powders;
(ii) Provides for high nanotube content (~10 to ~60 wt.%) with tailorable composition and properties;
(iii) Can be laminated with itself or other compatible materials: “thick” panels, surface or interlaminar modification;
(iv) Offers a suitable combination of multifunctional properties for EM shielding, flame resistance, heating, and other applications;

As described here, proof-of-concept has been achieved for continuous manufacturing of CNT-TPU fabrics based on an aerosol spray process. Efforts toward pilot-scale manufacturing and application studies are ongoing.

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