# ELECTRICALLY RESPONSIVE POLYURETHANE-CNT SHEETS FOR SENSING AND HEATING

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## ABSTRACT

Carbon nanotubes (CNTs) possess low density, unique geometry, as well as excellent mechanical, electrical, and thermal properties making them attractive for multifunctional enhancement of polymers. In this study, we developed multifunctional materials based on high CNT content thermoplastic polyurethane (TPU) nanocomposite sheets with electrical conductivity above 1000S/m and ultimate strains that can reach over 200%, making the material suitable for various applications where a combination of structural properties and electrical response is required. In addition to studying mechanical and electrical enhancement, the thermal-electrical response, strain sensing, and Joule heating capabilities were also studied. The high content of CNTs within TPU provides a robust network, which results in an ability to detect strains above 100% (vastly more than the <5% for metallic strain gauges) with a response that is more linear than traditional conductive polymer composites. The TPU/CNT sheets are also able to detect temperature changes and sense thermal related damage. The combination of mechanical strength, lightweight/porosity, and other functionalities shows promise for several multifunctional applications.

## 1 INTRODUCTION

Carbon nanotubes (CNTs) have been widely researched due to their exceptional mechanical, electrical, and thermal properties, while possessing low density and high aspect ratio. Reinforcement of thermoplastic polyurethanes (TPUs) with CNTs greatly improves their mechanical, electrical, and thermal properties, while maintaining, in some cases, a high failure strain [1, 2]. Additionally, the resulting nanocomposite material (CNT/TPU) can offer a wide range of multifunctional capabilities, such as strain sensing, environment sensing and joule heating.

Traditional metal foil based strain sensors have high sensitivity, but are unidirectional and cannot be embedded into structural materials [3]. As an alternative, a wider range of strain sensing has been achieved by depositing CNT networks onto a TPU substrate, effective for strains of up to 400% [4]. However, these sensors lack in multifunctionality. Dispersing CNTs inside an elastomer matrix has also shown varying levels of success (200% to 400% strain), but has non-linear electromechanical behavior due to a non-robust conductive network [5, 2]. Furthermore, creating multifunctional sensors often come at the expense of compromising its mechanical properties. The CNT/TPU composites developed in this study offer a robust network of nanotubes allowing a much more linear electromechanical response, while concurrently enhancing their mechanical and electrical properties. These materials offer several other advantages (e.g., heating capability and thermal-electrical response), which are the subject of the following sections.

# 2 MATERIAL PREPARATION AND EXPERIMENTAL PROCEDURES

## *2.1 Material Preparation*

Thermoplastic polyurethane (UAF 472 by Adhesive Films Inc.) and multi-walled carbon nanotubes (NC7000$^{TM}$ by Nanocyl) were used to prepare CNT/TPU nanocomposites, using a one-step filtration technique. CNTs and TPU were dispersed into a mixture of acetone and methanol, and then placed under bath sonification for 30 minutes. The resulting solution was filtered through a Teflon membrane, and then dried under compression. Details about material preparation can be found elsewhere [6].

## *2.2 Tensile testing*

A micro-tensile test frame (Fullam Substage Test Frame) was used to obtain the Young's modulus ($E$), ultimate tensile strength (*UTS*), and ultimate tensile strain ($\varepsilon_{max}$) for various compositions of CNT/TPU nanocomposite sheets. Five rectangular strips with dimensions 2 × 20mm of each material were cut using a razorblade, and tested. A gauge length of ~15mm and displacement rate of 5mm/min was used.

## *2.3 Thermal-electrical testing*

### *2.3.1 Temperature dependency test*

Samples of 2 × 30mm were cut into rectangular strips, and a conductive silver paste (DuPont 4929N) was used to attach electrodes at both ends of each sample. The temperature dependency tests were done by placing a sample in a convection oven, heating the sample to the testing temperature, and then cooled back down to 30°C for two cycles. A constant voltage of 0.25V was applied using a source-measure unit (Keithley 2635A) while measuring current, and a wireless thermocouple connected to a data acquisition software (TC central) was used to monitor the temperature.

### *2.3.2 Joule heating test*

Joule-heating experiments were done on 30 × 20mm rectangular samples with silver paste attached as electrodes (DuPont 4929N). A Source-measure unit (Keithly 2635A) was used to increment the voltage by 0.5V at intervals of 100 seconds until 9V or visible material degradation was reached. An infrared camera (FLIR SC8000 HS) was used to monitor the sample temperature.

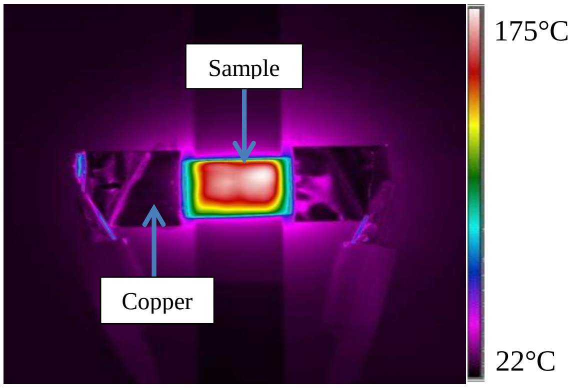

Figure 1: Experimental setup for joule heating

### 2.4 *Electro-mechanical testing*

Electro-mechanical testing was performed by sandwiching the specimen and a copper film electrode between two insulating sandpapers under the clamps of the micro-tensile test frame (Fullam Substage Test Frame. The copper electrodes were attached to electrical wires of a source-measure unit (Keithley 2635A). The cyclic tests were performed at a rate of 0.5 mm/min to 1% and 5% strain, and non-cyclic tests were continued until specimen failure.

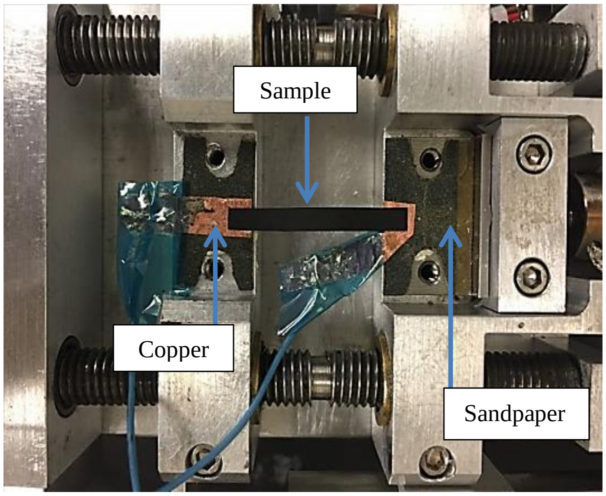

Figure 2: Experimental setup for strain sensing.

## 3 RESULTS AND DISCUSSION

### 3.1 *Mechanical and electrical properties*

The mechanical and electrical properties of various weight fractions of CNT/TPU and neat TPU and pristine CNT sheets are summarized in Table 1. As can be seen, the void content increases progressively with increasing CNT content suggesting a more porous morphology for higher CNT ratios, which is consistent with our SEM observations. The maximum modulus (0.6 GPa) occurs at a CNT:TPU ratio of approximately 1:1 (48:52), but at this composition the sheet lacks in UTS and stretchability for high strain applications. The in-plane conductivities of all the CNT/TPU nanocomposites are within the same order of magnitude of the neat CNT sheet (buckypaper). This suggests that TPU does not significantly affect the electrical conductivity. In fact, at 48wt% CNT (48:52 sample), the conductivity is slightly higher than that of pristine buckypaper, possibly due to a denser nanotube network after compression.

| CNT:TPU (wt ratio) | Density ($g/cm^3$) | Void (%) | *E* *(MPa)* | UTS (MPa) | ε fail (%) | σ (S/m) |
|---|---|---|---|---|---|---|
| **0:100** | 1.07 | - | 60±10 | 5.1±0.4 | >1500 | $<10^{-12}$ |
| **20:80** | 1.06 | 12 | 310±50 | 30±2 | 180±20 | 1000 |
| **35:65** | 0.96 | 26 | 380±60 | 29±1 | 61±7 | 1700 |
| **48:52** | 0.68 | 55 | 600±90 | 25±3 | 35±5 | 3100 |
| **86:14** | 0.29 | 82 | 80±10 | 1.6±0.2 | 4.2±0.7 | 2700 |
| **100:0** | 0.27 | 84 | 150±60 | 1.4±0.4 | 1.6±0.3 | 2600 |

Table 1 – Mechanical and electrical properties for various compositions of TPU/CNT

## *3.2 Strain sensing*

### *3.2.1 Sensing to failure*

Figure 3 shows the electro-mechanical response of two CNT/TPU nanocomposites (20:80 and 35:65) up to 120% strain (or specimen failure). The sensitivity of the material is characterized by the gauge factor (GF), which can be calculated using equation 1:

$$GF = \frac{\Delta R}{R_0 \varepsilon} = (1 + 2\nu) + \frac{\Delta \rho}{\rho_0 \varepsilon} \quad (1)$$

$\Delta R/R_0$ is the change in resistance, $\varepsilon$ is mechanical strain, $\nu$ is Poisson's ratio, and $\Delta\rho/\rho_0$ is change in resistivity. Both the 35:65 and 20:80 CNT/TPU batches showed a linear electrical response up to 60% strain, corresponding to a GF of roughly 1.9. At 60% strain the 35:65 nanocomposite failed, while the 20:80 nanocomposite showed a non-linear electrical response, increasing in sensitivity up to 120%, at which the GF was estimated at~ 3.5.

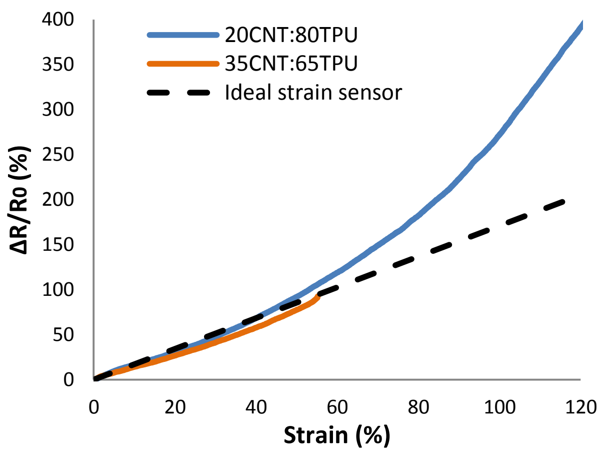


Figure 3 – Strain sensing to failure of CNT/TPU composite materials up to 120% strain.

### *3.2.2 Cyclic sensing*

Figure 4 presents the electro-mechanical response of two different CNT:TPU nanocomposites (20:80 and 35:65) and pristine buckypaper at 1% (a) and 5% (b) cyclic strain. Under 1% cyclic strain, 20:80 and 35:65 showed superior sensing capabilities compared to the neat buckypaper, with an initial gauge factor of 1.5 and 1, respectively. The resistance peaks of both neat buckypaper and nanocomposite materials decreased until the fifth cycle. After this, the response begins to stabilize for CNT/TPU sheets, while the pristine buckypaper continued to decrease in resistance. This suggests that the TPU helps by preventing the nanotube network from reordering/damaging. Under 5% cyclic strain, the 20CNT:80TPU and 35CNT:65TPU had initial GFs of 1.6 and 1.2 respectively. Due to a larger amount of plastic deformation compared to the 1% cyclic strain, only 3% of the strain was recovered after the first cycle. However, similar to the 1% loading, the resistance peaks stabilized approximately after the fifth cycle.

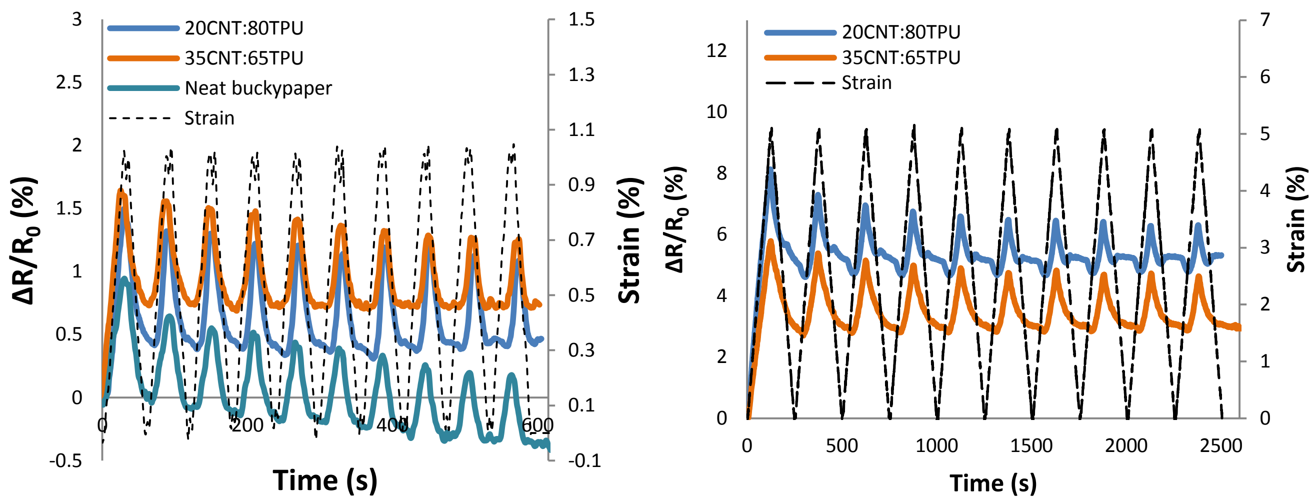


Figure 4: Electro-mechanical response of buckypaper sensors at (a) 1%, (b) 5% cyclic strain.

## ***3.3 Thermal response***

### *3.3.1 Temperature dependency results*

Figure 5 shows the cyclic thermal-electrical response of the 20:80 CNT/TPU up to 100°C and 150°C (a) as well as pristine buckypaper up to 160°C (b). The resistances of both materials decreased with increasing temperature, indicating a negative thermal coefficient of resistance (TCR) as is commonly observed with CNT networks. At roughly 40°C (Fig. 5a), the CNT/TPU temporarily showed a positive temperature coefficient (PTC). This phenomenon is known to occur in conducting composites, often near the glass transition temperature of the material [7]. This effect is strongly related to the thermal strain rate of the matrix, and can be greatly reduced if the heating rate is significantly decreased [8]. The buckypaper showed linear repeatable behavior with cyclic temperature change. The CNT/TPU showed repeatability up to 100°C, however, anything beyond this temperature resulted in a permanent change in the material (orange curve). After the first cycle past 100°C, the CNT/TPU showed repeatable behavior, and had a comparable TCR to neat buckypaper.

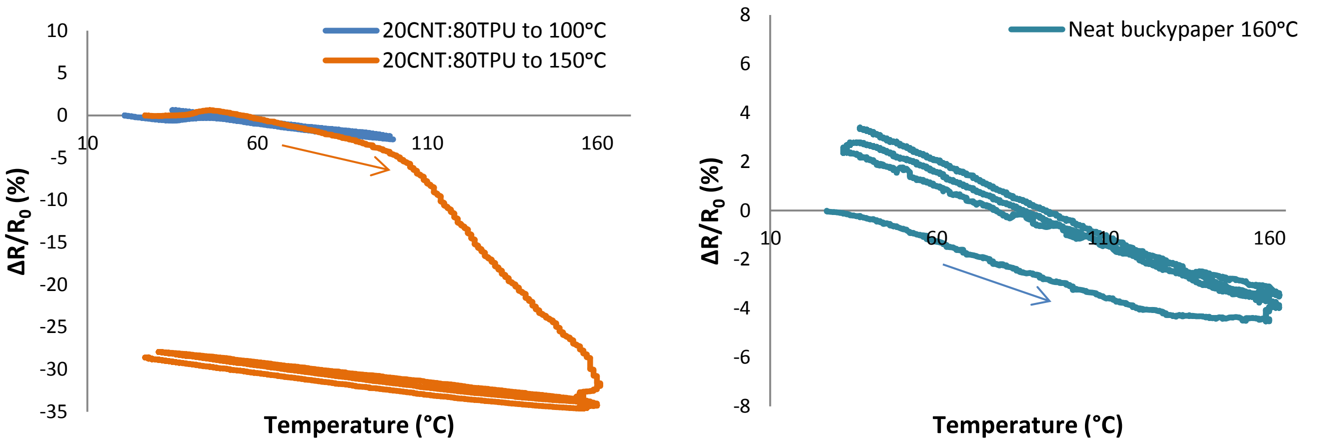


Figure 5: Temperature dependency of (a) 20:80 CNT/TPU to 100°C and 150°C and (b) neat buckypaper to 160°C

### *3.3.2 Joule heating*

Figure 6 shows the joule heating behavior of the 20:80 CNT/TPU and neat buckypaper suspended in air. Both the CNT/TPU and neat buckypaper were capable of reaching temperatures above 250°C. At temperatures below 40°C, the buckypaper was much more responsive to joule heating. This might be due to the resistance of the CNT/TPU temporarily increasing due to the PTC phenomenon that occurs around 40°C in Figure 6. Above 40°C the CNT/TPU showed a very similar trend to the buckypaper.

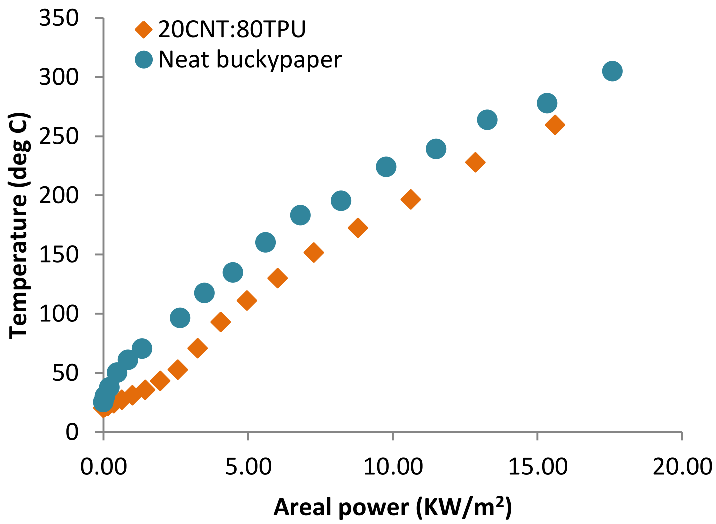


Figure 6: Joule heating of 20CNT:80TPU and neat buckypaper

## 4 CONCLUSION

A novel one-step filtration technique was successfully employed to fabricate a multifunctional CNT/TPU material with significant improvements in mechanical properties, and with electrical conductivity comparable to pristine CNT buckypaper. The CNT/TPU nanocomposites were demonstrated for strain sensing, temperature sensing, and Joule heating. The material was able to linearly detect strain (with GF of 1.9) up to 60%, and non-linearly up to 120% (GF 3.5). It also showed stable cyclic response to strain at both 1% and 5% after roughly the fifth cycle. The temperature dependency results showed repeatable linear response up to 100°C, but a permanent change occurred at higher temperatures. Additionally, the CNT/TPU was successfully heated to surface temperatures above 250°C, by Joule heating.

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