

# PRODUCTION OF POLYURETHANE/NANOTUBE COMPOSITES WITH TAILORABLE PROPERTIES AND FUNCTIONALITIES

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## ABSTRACT

Carbon nanotubes (CNTs) or boron nitride nanotubes (BNNTs) were used for the fabrication of high nanotube (NT) content polymer composites. NT/polyurethane composite sheets were fabricated by a scalable, one-step filtration method from a suspension of polyurethane (TPU)-modified nanotubes. The composition of the resulting NT/TPU composite sheets can be controlled through proper selection of the processing conditions. Hence materials with tailorable properties (e.g. porosity, density, stiffness, toughness) can be readily produced by this method. A comparative study of the influence of BNNTs and CNTs on the tensile, electrical and mechanical properties of NT/TPU composite sheets was undertaken. The tensile properties of the composite sheets were significantly enhanced over the unmodified TPU by incorporation of BNNTs and CNNTs. The nanocomposite sheets are flexible, robust and can be handled like conventional fabrics offering opportunities for the fabrication of hierarchical composite laminates. We explored the use of AFM to assess the CNT/TPU sheets unique morphology and the mechanical properties at the nano/microscale.

## 1 INTRODUCTION

The development of polymer nanocomposites is an important area of current nanotechnology and composite materials science. Light-weight, one-dimensional nanomaterials such as carbon nanotubes (CNTs) and boron nitride nanotubes (BNNTs) possess impressive physical, chemical and mechanical properties, and are promising candidates to be used as reinforcing agents for the development of enhanced multifunctional composite materials. Although BNNTs and CNTs share similar mechanical properties, they can impart different sets of functionalities in a composite material. CNTs are electrically conductive and are most-commonly employed in composites to improve the electrical conductivity of a matrix. On the other hand, BNNTs show transparency in the visible region

# PRODUCTION OF POLYURETHANE/NANOTUBE COMPOSITES WITH TAILORABLE PROPERTIES AND FUNCTIONALITIES

and are electrically insulating. Thus, BNNTs are very promising nano-fillers for insulating polymer composites. Additionally, BNNTs have higher resistance to oxidation and the ability to shield neutron radiation. By introducing nanotubes (NTs) into a polymer matrix, many properties can be improved at once, including mechanical, electrical, thermal and thermo-mechanical. Among polymers most widely used as adhesives and matrices, polyurethanes (PUs) stand out for their good adhesion and mechanical properties. Thermoplastic polyurethanes (TPU) have attracted great deal of attention for the fabrication of CNT-polymer composites [1-3]. However, it is still challenging to attain a simple and economical method that improves NTs dispersion and interfacial interaction with the matrix. We have developed a process for the fabrication of high NT-content composite sheets using a one-step solution method that is easy to scale-up and can be applied to different polymer matrices [4]. Here we show that NT/TPU materials with tailorable physical and mechanical properties, including significant enhancement in tensile properties and electrical conductivity are readily obtained by this method. A comparative study of the influence of CNTs and BNNTs with different purities and surface modification on the tensile, electrical and mechanical properties of NT/TPU composite sheets was undertaken.

## 2 EXPERIMENTAL

### 2.1 Materials

Multiwall carbon nanotubes (MWCNTs) were purchased from Nanocyl (Nanocyl NC7000 MWCNTs). The raw BNNT material was manufactured in-house from hexagonal boron nitride (h-BN) powder using an induction thermal plasma technique [5], and was purified by thermal and solvent treatments. BNNTs from two different purification stages (named P1 and P2 materials in Table 2) were used to prepare BNNT/TPU nanocomposites. Figure 1 shows SEM images of the pristine MWCNT and BNNTs from these two purification stages. Additionally, P2-BNNTs were functionalized with isocyanate moieties [6] to produced functionalized BNNTs (F-BNNTs). The thermoplastic ester-based polyurethane (TPU) sold as a film adhesive product UAF 472, was supplied by Adhesive Films, Inc.

### 2.2 Fabrication of NT/TPU nanocomposites

TPU and NTs were combined at different weight ratio (Table 1 and 2) in a solvent/non-solvent mixture using bath sonication and tip sonication to form a suspension. This suspension was filtered through a PTFE filter membrane with an average pore diameter of 1.2  $\mu\text{m}$ . After filtration, the nanocomposite sheets were sandwiched between sheets of parchment paper and dried flat at room temperature overnight. Residual solvent was removed at 75  $^{\circ}\text{C}$  in a vacuum oven. Table 1 and Table 2, respectively, summarize the MWCNT/TPU and BNNT/TPU sheets prepared in this study with different NT/TPU weight ratios in the recovered nanocomposite sheets.

# PRODUCTION OF POLYURETHANE/NANOTUBE COMPOSITES WITH TAILORABLE PROPERTIES AND FUNCTIONALITIES

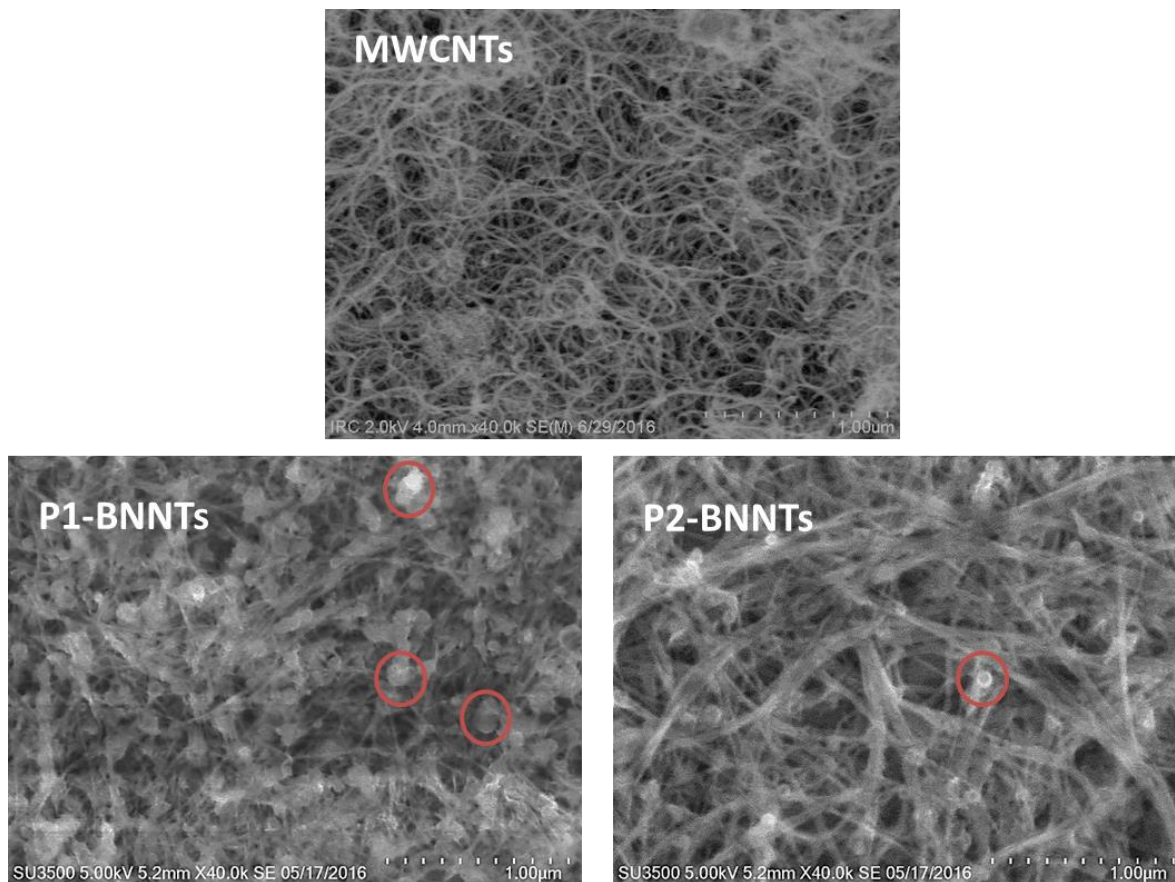


Figure 1. SEM images of MWCNTs and BNNTs from different purifications states (P1 and P2). Pink circles identify h-BN impurities

Table 1. Characteristics of CNT/TPU sheets prepared in an acetone/methanol mixture (Methanol 50 vol%)

Sample	TPU/MWCNT in solution	MWCNT/TPU sheet (wt. ratio)	Density (g/cm <sup>3</sup> )	Void (vol.%)
MWCNT-BP	0	100:0	0.25	84
CNPU45	1:1	55:45	0.57	63
CNPU55	1:1.5	45:55	0.29	55
CNPU65	1:2.5	35:65	0.81	32

# PRODUCTION OF POLYURETHANE/NANOTUBE COMPOSITES WITH TAILORABLE PROPERTIES AND FUNCTIONALITIES

Table 2. Characteristics of BNNT/TPU sheets prepared in a THF/methanol mixture at different vol % of the non-solvent (methanol)

Sample	BNNT Purification/ Functionalization	TPU/BNNT in solvent (weight ratio)	Solvents (Methanol vol.%)	BNNT/TPU sheet (wt%. ratio)	Density (g/cm <sup>3</sup> )	Void (vol.%)
BNNT-BP	P1 and P2	0	Methanol	100:0	0.38	81
P1-BNPU15	P1	1:5	THF/Methanol (40)	85:15	0.65	63
P1-BNPU20	P1	1:2	THF/Methanol (50)	80:20	0.86	49
P1-BNPU60	P1	1:2	THF/Methanol (60)	40:60	1.00	28
P2-BNPU60	P2	1:2	THF/Methanol (60)	40:60		
F-BNPU10	F-BNNTs	1:5	THF/Methanol (40)	90:10	0.64	64
F-BNPU20	F-BNNTs	1:2	THF/Methanol (50)	80:20	0.79	53
F-BNPU65	F-BNNTs	1:2	THF/Methanol (60)	40:65	1.29	5

\* P1 and P2 materials from different purification stages; F-BNNTs functionalized BNNTs

## 2.2 Characterization

Scanning electron microscopy (SEM) images were taken with a Hitachi SU3500 variable pressure SEM. Tensile testing was completed by using a micro-tensile test frame (Fullam Substage Test Frame). A minimum of five strips (~30x2mm) specimens of each material were tested at a displacement rate of 5mm/min and initial gauge length of ~20mm. Atomic force microscopy imaging and modulus mapping were carried out using the MultiMode AFM with the NanoScope V controller (Bruker Nano Surfaces Division, Santa Barbara, CA, USA), in Peak Force QNM mode. The peak force with which the tip taps the sample surface was always kept at the lowest stable imaging level of 200 – 400 pN. Silicon nitride ScanAsyst-Air AFM probes (Bruker AFM Probes, Camarillo, CA, USA) were used in all peak force feedback measurements. Their manufacturer specified typical tip diameter and spring constants are 2 nm and 0.4 N/m respectively. While images of sizes of up to 20 x 20 μm<sup>2</sup> were acquired to insure good homogeneity nanotube networks, all the images used to measure modulus were 500 nm x 500 nm<sup>2</sup> in size, acquired with the 512 x 512 pixel resolution, and the AFM probe cantilever was vertically oscillated at 2 kHz, at a lateral scan rate of 1 Hz. In this way the lateral pixel size is approximately 1 x 1 nm<sup>2</sup>. The Young's modulus values were analyzed in terms of the distribution of Derjagin-Muller-Toropov (DMT) moduli over the investigated area. In order to obtain reliable results of mechanical properties through AFM, the “relative calibration method” was adopted; details about the “relative method” can be found in the instrument manual provided by Gojzewski et al. [7]. Two reference samples were selected for calibration: polystyrene and polydimethylsiloxane gel with elastic

# PRODUCTION OF POLYURETHANE/NANOTUBE COMPOSITES WITH TAILORABLE PROPERTIES AND FUNCTIONALITIES

modulus of 2.7 GPa and 3.5 MPa, respectively. The calibration was always carried out before any measurements of the samples characterized.

A one-step filtration method was used to prepare NT/TPU sheets using a solvent/non-solvent mixture where the non-solvent induces TPU phase separation and immobilization on the NTs through Van der Waals interactions. NT/TPU composite sheets or fabrics (70-150  $\mu\text{m}$  thickness) are then recovered by filtration of the suspension. A higher affinity for TPU was observed for CNT than for BNNTs since, for the same vol.% of the non-solvent (methanol) in the solvents mixture, a lower TPU content was attained in BNNT/TPU sheets than in CNT/TPU sheets (e.g. samples CNPU55 and P1-BNPU20). Figure 2 shows photos of the BNNT/TPU and CNT/TPU nanocomposite sheets fabricated by the one-step filtration method. Semitransparent sheets can be obtained when BNNTs are used, showing its potential for the development of high NT-content nanocomposites where a level of transparency is also desired. In both cases, BNNT/TPU and CNT/TPU, the sheet density increases with increasing TPU content (Table 1 and 2) and the void content decreases from the values observed for pristine NT sheets or buckypapers (BP). However, the nanocomposites are still porous. Interestingly, for similar NT/TPU ratios, the void contents of BNNT/TPU sheets are lower than those of CNT/TPU sheets (e.g. samples P1-BNPU60 and F-BNPU65 compared to CNPU65). This originated from a different packing of the nanotubes in the nanocomposite sheets.



Figure 2. Photos of BNNT/TPU (F-BNPU65) and CNT/TPU nanocomposite sheets (70-150  $\mu\text{m}$  thickness)

SEM images of the surface of BNNT/TPU (F-BNPU65) and CNT/TPU (CNPU65) sheets are shown in Figure 3. In both cases a high content of nanotubes is observed embedded with the TPU matrix. However, the morphologies are slightly different with CNT/TPU samples showing a more defined, fiber-like morphology with bigger diameter than in BNNT/TPU samples.



# PRODUCTION OF POLYURETHANE/NANOTUBE COMPOSITES WITH TAILORABLE PROPERTIES AND FUNCTIONALITIES

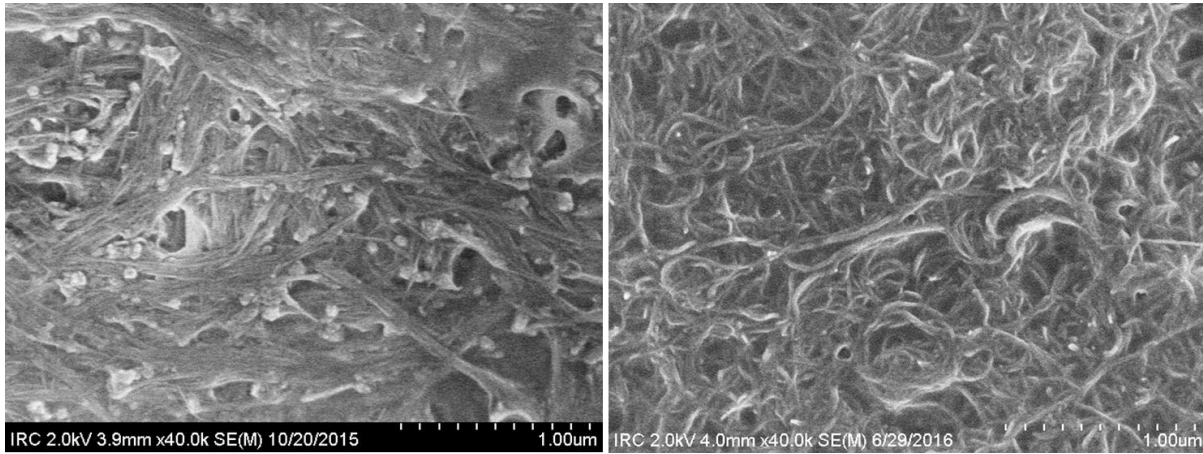


Figure 3. SEM images of the surface of BNNT/TPU (F-BNPU65) and CNT/TPU (CNPU65) sheets

Table 3. Tensile properties of CNT/TPU and BNNT/TPU composite sheets

Sample	Young's Modulus (MPa)	Tensile Strength (MPa)	Strain at Failure (%)	BNNT/TPU sheet (wt. ratio)	Void content (vol.%)
TPU	120	4 <sup>1,2</sup>	580 <sup>2</sup>	0:100	0
CNPU45	575 ± 89	21 ± 3	39 ± 9	55:45	63
CNPU55	630 ± 87	26 ± 2	44 ± 4	45:55	55
CNPU65	1270 ± 230	41 ± 2	85 ± 9	35:65	32
P1-BNPU15	510 ± 26	2 ± 1	0.5 ± 0.2	85:15	63
P1-BNPU20	490 ± 20	4 ± 1	2 ± 0.5	80:20	49
P1-BNPU60	245 ± 35	12 ± 5	80 ± 5	40:60	28
P2-BNPU60	1580 ± 259	20 ± 2	110 ± 40	40:60	
F-BNPU10	2125 ± 260	16 ± 1	2 ± 0.3	90:10	64
F-BNPU20	2230 ± 232	22 ± 1	6 ± 1	80:20	53
F-BNPU65	1950 ± 99	27 ± 3	80 ± 30	40:65	5

<sup>1</sup>Reported by the manufacturer

<sup>2</sup> Stress at 100% strain

# PRODUCTION OF POLYURETHANE/NANOTUBE COMPOSITES WITH TAILORABLE PROPERTIES AND FUNCTIONALITIES

The tensile properties of CNT/TPU sheets and BNNT/TPU sheets containing BNNTs from different purification stages (P1 and P2) as well as functionalized BNNTs (F-BNNTs) are summarized in Table 3. Buckypapers fabricated with NTs alone (BNNT-BP and CNT-BP) displayed similar properties (elastic modulus  $\sim 100$ -300 MPa, ultimate strength  $\sim 1$ -2 MPa, failure strain  $\sim 0.5$ -1%). Note that the neat TPU baseline did not fail within the displacement limit of our test. The TPU used in this study is a thermoplastic rubber with manufacturer reported values of 34 MPa, 4 MPa and 8 MPa for the tensile strength, stress at 100% strain and stress at 300 % strain, respectively. CNT/TPU sheets fabricated by the one-step filtration approach show higher strength and stiffness than either neat buckypaper or TPU on their own, along with a trend of increasing strength and stiffness with increasing TPU content. In the case of BNNT/TPU sheets the same trend was observed in strength but not for the Young's modulus. Significantly lower tensile properties were obtained for BNNT/TPU sheets containing the P1-BNNT material. As shown in Figure 1 P1-BNNT contains a larger quantity of non-BNNT material (identified as h-BN-like cages). When the purity of the material is improved the properties of the BNNT/TPU significantly increase. However, when compared with a sample of similar composition containing CNTs, the values of tensile strength are still lower for nanocomposite sheets containing BNNTs (e.g. samples P2-BNPU60 and CNPU65 in Table 3). These results support our observations above indicating that there is a stronger interaction between CNTs and TPU, which leads to a higher improvement in tensile properties. In order to improve the surface interaction between BNNTs and TPU the BNNTs were modified with isocyanate moieties. As seen in Table 3, the tensile properties increased significantly after this modification. The highest values for Young's Modulus are observed when functionalized BNNTs are used, while the strength and failure strain also improved showing the same trend previously observed with increasing TPU content. A summary including tensile properties of the different NT/TPU sheets at the highest TPU content achieved in this study ( $\sim 60$  wt% TPU) is shown in Figure 5. The electrical conductivity of the CNT/TPU sheets was also evaluated as a function of the TPU content. Values in the 2500-2200 S/m range were observed, which were comparable to a pristine BP made of unmodified CNTs (2400 S/m).

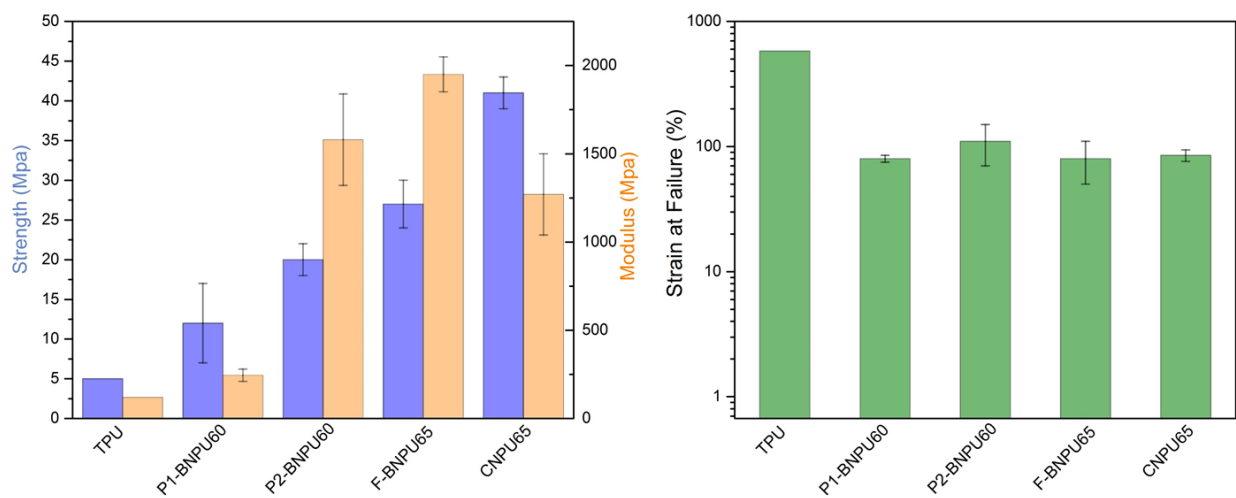


Figure 5. Comparison of the tensile properties of the different NT/TPU sheets at the highest TPU content achieved in this study

# PRODUCTION OF POLYURETHANE/NANOTUBE COMPOSITES WITH TAILORABLE PROPERTIES AND FUNCTIONALITIES

Peak Force QNM mode atomic force microscopy (AFM) was conducted on CNT/TPU composites and pure TPU in order to correlate experimental tensile tests (macroscale) with the elastic modulus at the nano/microscale. Sample's module maps for neat TPU and CNPU45 are shown in Figure 6a and b, respectively. Polyurethane elastomers are a broad family of segmented block copolymers consisting of hard crystalline segments (HS) dispersed between flexible amorphous segments (SS). The unmodified TPU (Figure 6a) clearly show well separated phases in the form of ribbon-like hard domains, dispersed in the SS phase matrix. The modulus profiles (Figure 6c) for neat TPU shows a sharp elastic modulus distribution (from 9 to 100 MPa) with maximum at 59 MPa. CNPU composites show a more broad distribution from 9 to 460 MPa and 9 to 250 MPa for CNPU45 and CNPU65, respectively. The trend of increasing Young's modulus with increasing TPU content at the macroscale (Table 3) was not observed by AFM. Although both CNPU composites show higher effective modulus than the unmodified TPU (Figure 6c, maximum at 220 MPa and 100 MPa for CNPU45 and CNPU65, respectively), CNPU65 shows a lower value than CNPU45. Additionally, the results obtained from uniaxial macroscopic tensile tests are significantly higher than those determined by AFM. It is worth pointing out that the AFM measurements were carried out on the surface of the films and only several micron sizes of samples were analyzed. More experiments are being conducted to better understand these results.

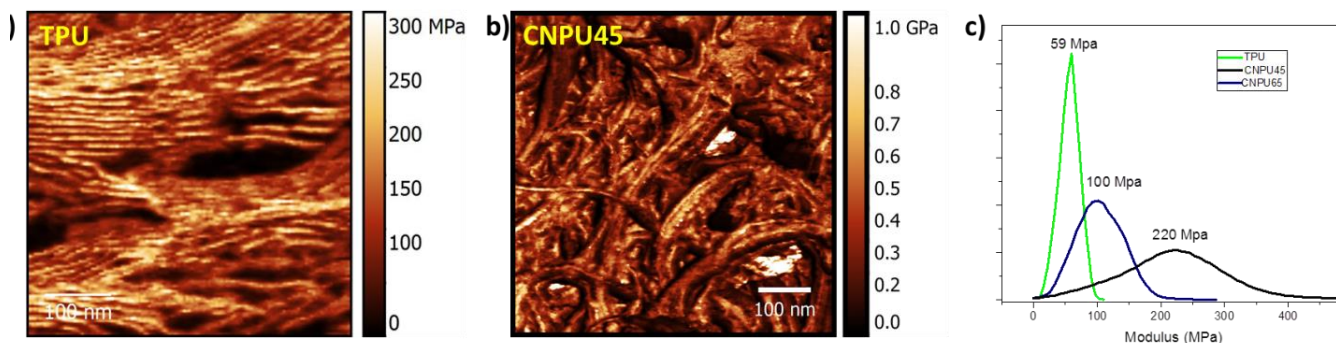


Figure 6. DMT modulus maps of TPU (a), CNPU45 (b) and distributions of DMT modulus (c) analyzed from the respective modulus maps for TPU, CNPU45 and CNPU65.

## 3 CONCLUSION

NT/TPU composite sheets with high content of nanotubes (CNTs and BNNTs) were successfully fabricated by a one-step filtration method. A trend of increasing strength and stiffness with increasing TPU content was observed. As expected, the purity of the BNNT material had a significant effect in the tensile properties of the BNNT/TPU nanocomposites. However, regardless of the BNNT purity level, higher overall tensile properties were obtained for CNT/TPU sheets when pristine nanotubes were employed suggesting a stronger interaction of these CNTs with polyurethane than the pristine BNNTs. At the highest TPU content, CNT/TPU nanocomposite sheets showed significant improvement in stiffness (up to 1.3 GPa) and strength (41 MPa), and high failure strain (85 %). Electrical conductivity values in the 2500-2200 S/m range were achieved in the TPU/CNT with little



# PRODUCTION OF POLYURETHANE/NANOTUBE COMPOSITES WITH TAILORABLE PROPERTIES AND FUNCTIONALITIES

dependency on the content of the insulating TPU matrix. After functionalization of the purified BNNTs with a reactive moiety, the highest improvement in stiffness was obtained (~100% improvement compared to CNT/TPU) with ductility values comparable to CNT/TPU sheets. We are using AFM to assess the CNT/TPU sheets unique morphology and to correlate the trend observed in tensile properties with the mechanical properties measured by AFM at the nano/microscale.

## 4 REFERENCES

- [1] J.H. Han, H. Zhang, M.J. Chen, G.R. Wang, Z. Zhang. "CNT buckypaper/thermoplastic polyurethane composites with enhanced stiffness, strength and toughness" *Composites Science and Technology*, Vol. 103, pp 63–71, 2014.
- [2] P. Russo, D. Acierno, G. Marletta, G. L Destri, "Tensile properties, thermal and morphological analysis of thermoplastic polyurethane films reinforced with multiwalled carbon nanotubes" *European Polymer Journal*, Vol. 49 pp. 3155–3164, 2013.
- [3] F. M Blighe, W. J. Blau, J. N. Coleman "Towards tough, yet stiff, composites by filling an elastomer with single-walled nanotubes at very high loading levels" *Nanotechnology*, Vol. 19 pp. 415709-415716, 2008)
- [4] K. S. Kim, M. B. Jakubinek, Y. Martinez-Rubi, B. Ashrafi, J. Guan, K. O'Neill, M. Plunkett, A. Hrdina, S. Lin, S. Denommee, C. Kingston, B. Simard, "Polymer nanocomposites from free-standing, macroscopic boron nitride nanotube assemblies" *RSC Advances*, Vol. 5, pp. 41186, 2015.
- [5] K.S. Kim, C.T. Kingston, A. Hrdina, M.B. Jakubinek, J. Guan, M. Plunkett, B. Simard "Hydrogen-Catalyzed, Pilot-Scale Production of Small-Diameter Boron Nitride Nanotubes and Their Macroscopic Assemblies" *ACS Nano*, Vol. 8, pp 6211-6220, 2014.
- [6] S. J. Zhou, C. Y. Ma, Y.Y. Meng, H. F. Su, Z. Zhu, S. L. Deng, S. Y. Xie "Activation of boron nitride nanotubes and their polymer composites for improving mechanical" *Nanotechnology* Vol. 23 pp. 055708- 055716, 2012.
- [7] H. Gojzewski, B. Imre, C. Check, R. Chartoff, and J. Vancso, "Mechanical mapping and morphology across the length scales unveil structure-property relationships in polycaprolactone based polyurethanes," *Journal of Polymer Science, Part B: Polymer Physics*, vol. 54, pp. 2298–2310, 2016