

THERMALLY CONDUCTIVE MELT-PROCESSABLE POLYIMIDE HBN MICRO-COMPOSITES FOR HIGH TEMPERATURE ELECTRICAL INSULATION APPLICATIONS

Witold K. Fuchs¹, Robin Weaver², Gabriel Antomattei-Alejandro³, Tiffany S. Williams¹,
Baochau N. Nguyen⁴

1 – NASA John H. Glenn Research Center
Cleveland, Ohio/USA

2 – NASA Internship Program/ Auburn University
Cleveland, Ohio/USA

3 – NASA Internship Program/ University of Puerto Rico – San Piedras
Cleveland, Ohio/USA

4 – University Space Research Association (USRA)
Cleveland, Ohio/USA

ABSTRACT

Thermoplastic polymers exhibit excellent dielectric properties and manufacturing robustness. These properties mark thermoplastics as competitive material candidates for electrical insulation applications. However, the high-temperature performance of most thermoplastics is insufficient to meet the electrical wiring requirements for next-generation air and space transportation engineering designs, with continuous operation temperature requirements of up to 200 °C among other design requirements. Furthermore, the low thermal conductivity (κ) of polymers as a material class leads to heat trapping within wires which can amplify thermal stresses. As a result, there is a need to investigate candidate thermoplastic systems for their high temperature, dielectric, and κ performance.

The goal of this work was to develop and characterize high operating temperature, melt processable, and thermally conductive thermoplastic electrical insulation materials systems to improve thermal management in high power density electric motors. Thermoplastic polyimide (TP PI) composites with up to 25 wt% micro-hBN were compounded and injection molded. The resultant composites exhibited good thermal stability with T_g s of 276 °C, mechanical robustness, and improvements in thermal conductivity by up to 70% while maintaining dielectric performance. A further post-processing step was demonstrated which again increased thermal conductivity to a total 110% improvement.

Keywords: polyimide, thermal conductivity, dielectric, electrical insulation
Corresponding author: Witold.k.fuchs@nasa.gov

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SAMPE Conference Proceedings. Long Beach, CA, May 20-23, 2024. Society for the Advancement of Material and Process Engineering – North America.

(DOI will be added by SAMPE)

1. INTRODUCTION

Power density requirements of next-generation air and spacecraft necessitate the development of electrical insulation systems that can support the new technologies. Polymers are typically used for electrical insulation systems due to their robust dielectric, mechanical, and thermal properties. [1] Contemporary high temperature electrical insulations are typically comprised of some structure comprised of fluorinated polymers such as polytetrafluoroethylene or fluorinated ethylenepropylene along with a polyimide (PI) tape. Although current PI tape technologies have high temperature performance, the ceiling temperature of the overall system can become limited due to the adhesive layer used to bond the PI tape to the insulation core. Therefore, a melt processable PI with high service temperatures is of interest as an electrical insulation candidate material. Additionally, melt processing enables facile dispersion of fillers within a polymer matrix which can impart additional functionality such as thermal conductivity.

Polymers generally exhibit very low thermal conductivity (κ). However, more thermally conductive polymer products are desirable given the added heat-wicking functionality high κ imparts. Several filler types have been used to improve κ of polymer composites. [2] Of these, boron nitride is particularly desirable due to its robust performance metrics and dielectric performance. [3,4] Hexagonal boron nitride (hBN) is a commercially available form of BN with platelet geometry. Previous research has demonstrated hBNs effects on polymer composite κ . [5] However, in addition to investigating a new polymer matrix, there is limited information available regarding the effects of hBN on other key polymer composite properties such as processability and mechanical performance.

In this article, a micron-size hBN was incorporated into a melt-processable thermoplastic polyimide trade name Aurum®* (TP PI) through twin-screw extrusion. Trend behavior from high density polyethylene (HDPE) experiments was used to down-select concentrations of interest for TP PI/hBN composites. Extruded films were characterized without further post processing. Extruded filament was pelletized and used for injection molding of test specimens. Composite processability was evaluated using rheology.

2. EXPERIMENTATION

2.1 Materials*

High density polyethylene (HDPE) was purchased from Millipore Sigma. Aurum® PL500A thermoplastic polyimide (TP PI) was purchased from Barplast LLC. PT180 hBN (mean particle size: 6-9 μm) was purchased from Momentive Technologies. PT180 hBN is described as a mixture of nano and micro sized particles. [6]

2.2 Methods

2.2.1 Film extrusion

Polymer micro composite films were extruded using a Thermo Fisher Scientific high temperature Process-11 twin-screw extruder equipped with a sheet extrusion die and a film take-up accessory. [5] The temperature profiles used for HDPE and TP PI extrusion are listed in **Table 1** and **Table 2**, respectively. Polymer and additive were added in zone 1 using single-screw feeders. Screw speed was set to 90 RPM. Additional heating was provided to the film die during polyimide extrusion by wrapping the film die in fiberglass-insulated heating tape. Average residence time

Table 1. Hopper-to-die temperatures for extruded HDPE and HDPE-hBN composite tapes.

Zone #	Film Die	Interface	Zone 8	Zone 7	Zone 6	Zone 5	Zone 4	Zone 3	Zone 2
Set (°C)	140 °C	140 °C	140 °C	140 °C	160 °C	160 °C	170 °C	180 °C	180 °C
Actual (°C)	140 °C	140 °C	140 °C	140 °C	160 °C	160 °C	170 °C	172 °C	151 °C

Table 2. Hopper-to-die temperatures for extruded TP PI and TP PI-hBN composite tapes.

Zone #	Film Die	Interface	Zone 8	Zone 7	Zone 6	Zone 5	Zone 4	Zone 3	Zone 2
Set (°C)	390 °C	390 °C	390 °C	390 °C	400 °C	400 °C	410 °C	410 °C	410 °C
Actual (°C)	390 °C	390 °C	390 °C	390 °C	400 °C	400 °C	410 °C	372 °C	283 °C

confirmed to be one minute. Three-minute purges were used between collection of loading levels to minimize cross-contamination between settings.

2.2.2 Thermoplastic annealing

Polyimide and HDPE extruded films were annealed and flattened to ensure good contact with the probes/sensors used for κ and dielectric analyses. Polyimide samples were placed between steel plates at room temperature conditions, followed by heating to 302 °C with an isothermal hold for 30 minutes. Then, the samples were cooled to room temperature using a 1-hour cooling ramp. Then, the samples were cooled to room temperature using a three-hour ramp. HDPE samples were annealed by placing between steel plates and heating to 93 °C using a two-hour ramp, followed by a one hour isothermal hold, then cooling back down to room temperature over twenty minutes. Kapton® (HN grade) was used as a non-stick layer between the steel plates and the samples during annealing and crystallization processes.

2.2.3 Scanning electron microscopy

Scanning electron microscopy (SEM) microscopy was performed using a MAIA3 TESCAN. Energy dispersive x-ray spectroscopy (EDS) was performed using an Oxford Instrument at 15.0 mm WD. Samples were cryo-fractured after immersion in liquid nitrogen until equilibration. Cryo-fractured surfaces were coated with 10 nm platinum before examination.

2.2.4 Thermal and thermomechanical analyses

Hexagonal BN loading levels were confirmed by thermogravimetric (TGA) char yield analysis at 900 °C, performed in triplicate, using a TA instruments Q50 TGA. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) characterization were performed using TA instruments Q1000 DSC and Q800 DMA. All analyses were performed in triplicate with statistically representative results presented.

2.2.5 Rheological analyses

Rheological analyses were performed using an Ares G-2 rheometer equipped with stainless steel 25 mm parallel plates and the polymer pellet loading accessory. Samples were loaded, heated to their melting point, then compressed to a 1.05 mm gap and trimmed. After trimming the gap was set to 1.00 mm and the sample was thermally conditioned at the starting temperature for 30 seconds prior to initiating the analytical run. Auto tension and auto strain were applied. Standard oscillatory temperature ramp and frequency sweep settings were used to conduct the analyses.

2.2.6 Thermal conductivity analysis

Thermal conductivity analyses were conducted using a Trident modified transient plane source method instrument manufactured by C-therm. Post-annealing samples were analyzed using deionized water as a contact agent. A 500 g weight was placed on top of samples to ensure good contact with the sensor. Measurements were collected in quintuplicate. The transient plane source method measures through-plane (\perp) κ , rather than in-plane (\parallel) κ . Through-plane κ is defined as perpendicular to the direction of polymer melt flow, where $\parallel \kappa$ is defined as parallel to the direction of polymer melt flow.

2.2.7 Dielectric breakdown and dielectric withstand voltage (DWV) analyses

Dielectric analyses were performed using a custom-made Eaton dielectric breakdown rig conforming to the ASTM D149-09 Standard Test Method for Dielectric Breakdown Voltage and Dielectric Strength of Solid Electrical Insulating Materials at Commercial Power Frequencies. [7] Round, ~ 6.38 mm probes were used. All samples were tested in silicone dielectric oil. The instrument was set to operate in DC. Samples were wiped down with IPA and air-dried for 5 minutes prior to analysis. Care was taken to avoid forming bubbles around the sample during insertion into the oil medium. Measurements were recorded in triplicate.

3. RESULTS

Given the relative novelty of both the polymer matrix and filler particle a decision was made to replicate the experiment in a facile and inexpensive demonstration system using HDPE. HDPE was selected as similarly to TP PI it is a semi-crystalline polymer, but the ease of manufacturing processes with this material helped ensure a more idealized result. Trend behavior from HDPE experiments was used to down-select concentrations of interest for TP PI/hBN composites.

3.1 Polyimide matrix characterization

Thermogravimetric analysis of TP PI demonstrated the material exhibits two degradation events when heated in an air atmosphere (**Figure 1a**). The onset of thermo-oxidative decomposition (T_d)

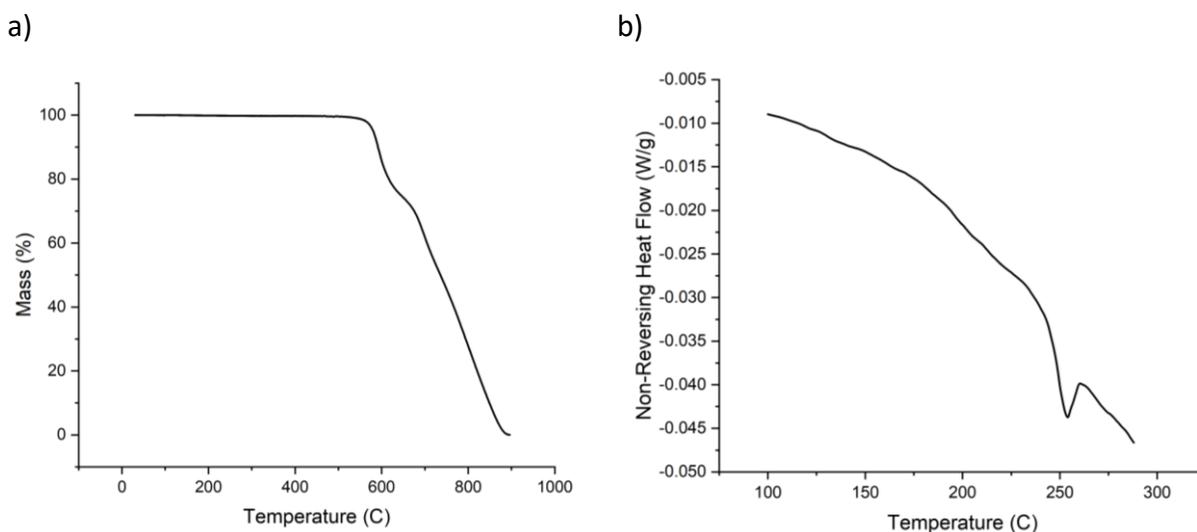


Figure 1. a) TGA trace of neat TP PI in air environment exhibiting two degradation events. Onset of degradation ($T_{98\%}$) = 564 °C and a secondary event at approximately 660 °C; b) DSC trace of TP PI exhibiting a T_g at 254 °C.

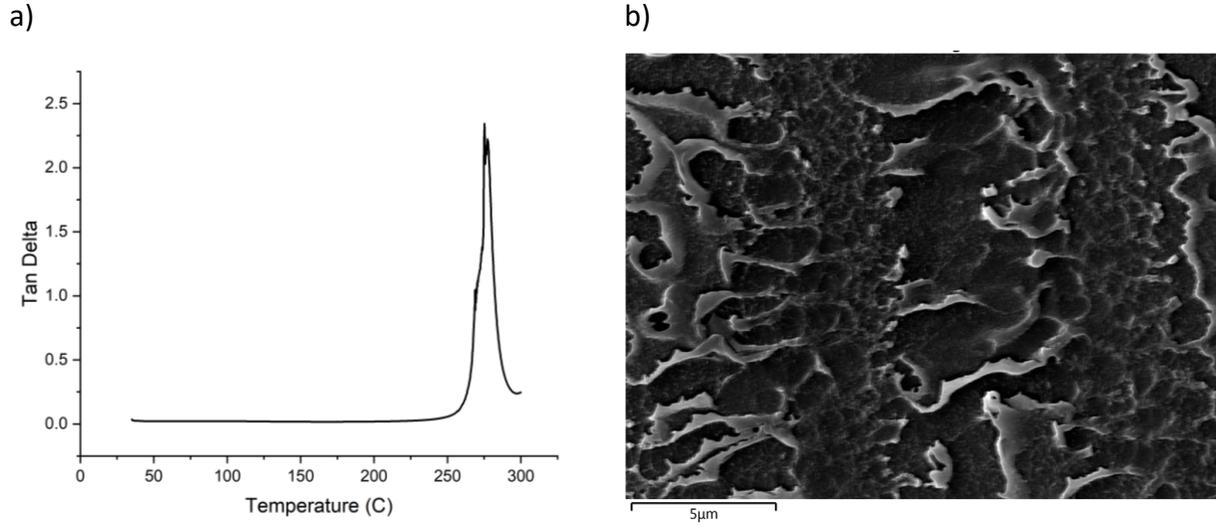


Figure 2. a) DMA trace of TP PI exhibiting a $\tan(\delta)$ peak at 276 °C; b) cryo-fractured cross-sectional image of extruded TP PI tape.

was measured at 564 °C. A secondary degradation event was measured at approximately 660 °C. Thermogravimetric char analyses at 900 °C were used to confirm predicted hBN concentrations in the composites. Differential scanning calorimetry analysis of TP PI demonstrated a T_g at 254 °C (**Figure 1b**). Interestingly, DMA analysis of the peak maximum of the $\tan \delta$ for TP PI showed a T_g of 276 °C (**Figure 2a**). Typically, a difference of approximately 10 °C is to be expected between DSC and DMA measurements, with DMA measurements trending higher. It was noted that TP PI exhibited a delta of approximately 20 °C between the two measurements. SEM analysis of extruded and cryo-fractured samples revealed smooth material surfaces free of manufacturing defects such as voids or foreign debris (**Figure 2b**).

3.2 Thermally conductive hBN/ HDPE and hBN/polyimide composites

HDPE composites with a range of concentrations of hBN were extruded and loading levels were assessed by TGA. Films were annealed to improve accuracy of measured through-plane (\ddagger) κ . Room-temperature $\ddagger \kappa$ results demonstrated an exponential increase in $\ddagger \kappa$ with increasing hBN concentration when extruded using the conditions described in this manuscript. Significant rate changes in $\ddagger \kappa$ were observed above approximately 20 wt% hBN (polynomial fit; $R^2 = 0.988$). (**Figure 3a**). Although HDPE composites with greater than 30 wt% hBN were successfully extruded, the resultant material was deemed too brittle for the intended application. Similar trends in brittleness were observed for TP PI and its composites. The extruded composites demonstrated

Table 3. Through-plane (\ddagger) thermal conductivity (κ) measurements of extruded composite tapes with differences relative to neat polymer κ indicated (Δ).

HDPE					TP PI				
Select hBN concentrations		\ddagger Thermal conductivity			Select hBN concentrations		\ddagger Thermal conductivity		
Weight %	\pm	W/mK	\pm	Δ	Weight %	\pm	W/mK	\pm	Δ
0	-	0.44	0.01	-	0	0	0.31	0.01	-
14.3	1.7	0.51	0.01	16%	10.5	1.9	0.41	0.01	32%
28.2	0.2	0.64	0.02	45%	17.8	0.8	0.43	0.04	39%
37.3	0.1	0.80	0.03	82%	23.6	1.3	0.49	0.01	58%

similar trends of κ improvement as HDPE composites within the studied range (**Figure 3a**). Notably, TP PI / hBN composites exhibited a larger change in κ relative to HDPE (45% improvement compared to 82% improvement at similar concentrations, respectively; **Table 3**).

Dielectric strength of a material directly affects the minimum insulation thickness necessary to achieve suitable voltage ratings and therefore system weight. Generally, polymer/hBN composites exhibit modest increases of dielectric strength with increasing hBN filler content. [4,8-10] However, some composites are reported to exhibit a decrease in dielectric strength with increasing hBN loadings or above certain hBN loading levels, highlighting the need to assess each material system and process separately. [4,10] The extruded hBN/HDPE composites studied within this work exhibited a significant linearly increasing trend in dielectric strength as a function of hBN concentration when measured in oil and under DC voltage. (**Figure 3b**). In contrast, TP PI/hBN composites exhibited a parabolic trend in dielectric strength increase, with a peak maximum dielectric strength observed at approximately 12 wt% hBN.

It was observed during extrusion experiments the significant effect of hBN incorporation on material specific strength. Furthermore, small adjustments in hBN concentration resulted in notable increases in extruder torque, with some high concentrations requiring elevated temperatures to process. As demonstrated in **Figure 4a** and **Figure 4b**, rheological evaluations of the extrudates were performed to understand the effect of hBN incorporation more fully on composite processability. It was observed that the 24.1 wt% hBN composite exhibited approximately 2x the complex viscosity than neat HDPE at lower melt temperatures (**Figure 4a**). Furthermore, more than 18 wt% of hBN appeared to introduce a high-temperature plateau in

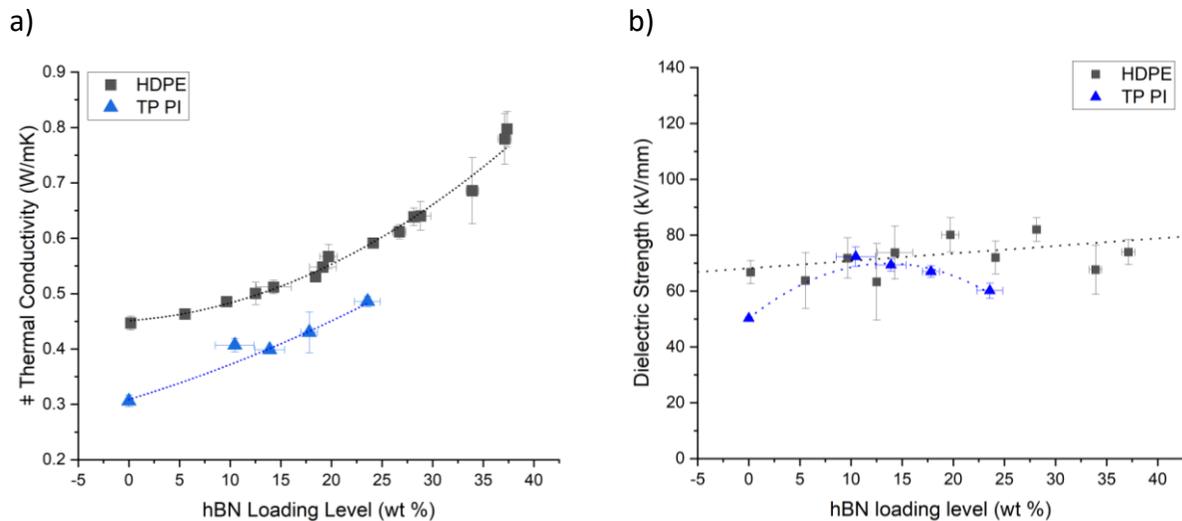


Figure 3. a) Room temperature thermal conductivity (κ) analyses of extruded HDPE and TP PI films. Thermal conductivity measured in the through-plane (\ddagger) direction; b) room-temperature dielectric strength results of extruded composite films in oil medium subject to DC voltage.

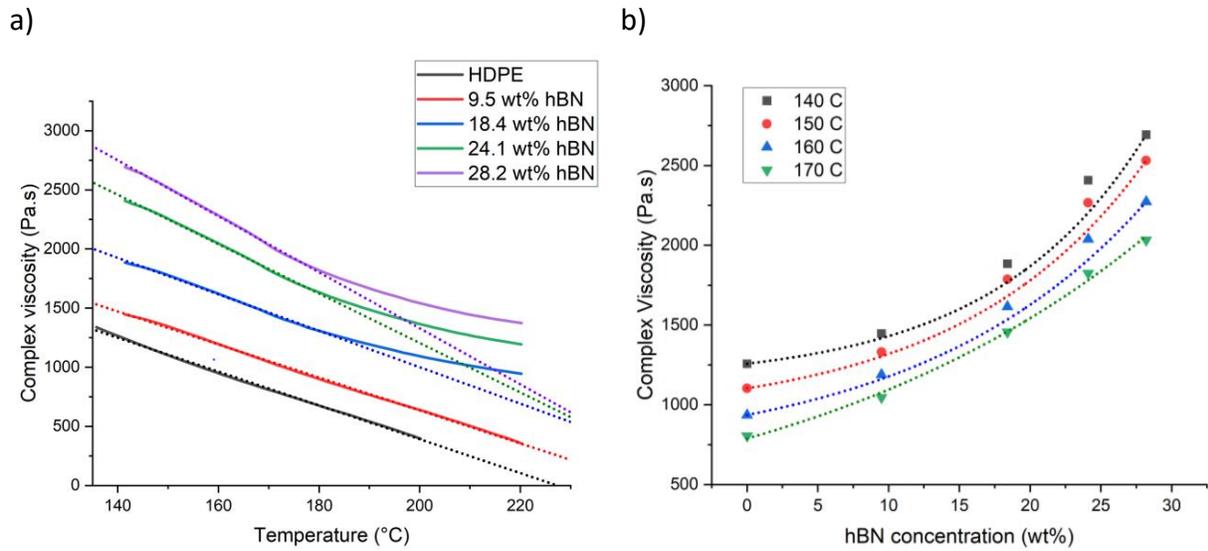


Figure 4. a) Temperature sweeps of HDPE/PT180 composites with linear lines of best fit indicating magnitude of discontinuous viscosity behavior; b) HDPE's complex viscosity response as a function of PT180 incorporation as seen at different temperatures.

viscosity reduction which could increase risk of unsuitable processing conditions at high hBN loading levels (**Figure 4b**). Therefore, based on the sum of these results and in combination with its corresponding κ and dielectric strength results seen in **Figure 3a** and **Figure 3b**, TP PI composites with $10 \text{ wt}\% < \text{hBN} < 30 \text{ wt}\%$ were selected for further study. Extruded TP PI composites with hBN exhibited seemingly roughened cryo-fractured surfaces, with visually distinct platelets confirming hBN presence in the composites and indicating a preference to shear-align in the flow direction (**Figure 5a**). The nitrogen-rich areas of extruded TP PI/hBN composites mapped using EDS indicated the presence of hBN in the fabricated tapes (**Figure 5b**).

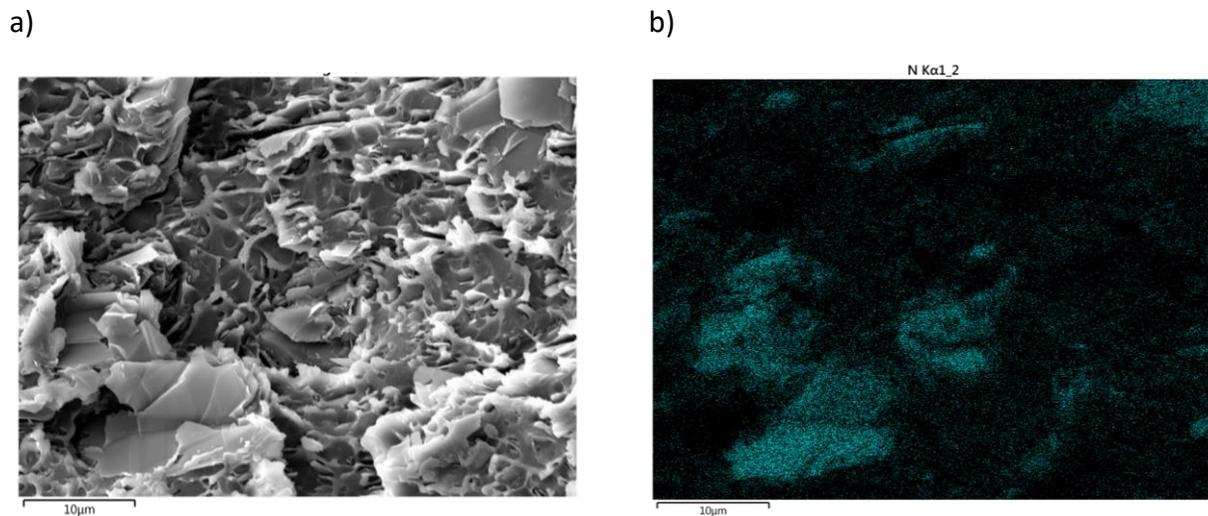


Figure 5. a) SEM micrograph of extruded and cryo-fractured TP PI film composites with 23.6 wt% hBN b) EDS scan of the same area demonstrating local nitrogen-rich and poor regions corresponding to hBN and TP PI, respectively.

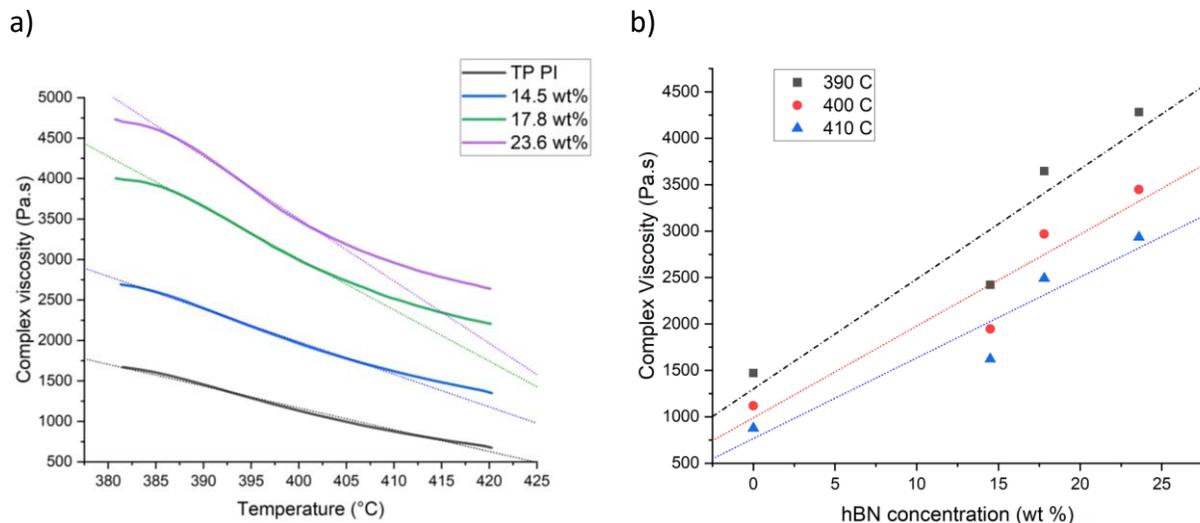


Figure 6. Rheological results of TP PI/PT180 hBN composites

Similar to the experience with HDPE/hBN, TP PI composites with hBN exhibited notably higher specific strength. Additional heating using fiberglass insulated heating tape had to be applied to the film die to reduce strain on the extruder to an acceptable level. Rheological analysis was performed to further investigate these experimental observations. The trend observed in HDPE was confirmed in TP PI that hBN incorporation greater than approximately 15 wt% resulted in non-linear viscosity decreases with increasing temperature (**Figure 6a**). Unlike HDPE, hBN incorporation exhibited a more significant effect on composite viscosity in TP PI (**Table 4** and **Table 5**). High (approximately 23.6 wt%) hBN concentrations in TP PI resulted in increases in viscosity as high as +300%.

Table 4. HDPE rheology results

hBN Weight % Temperature	140	Δ	150	Δ	160	Δ	170	Δ
0	1257		1103		936		805	
9.5	1447	+ 15%	1331	+ 21%	1189	+ 27%	1045	+ 30%
18.4	1884	+ 50%	1787	+ 62%	1615	+ 72%	1456	+ 81%
24.1	2408	+ 91%	2267	+ 105%	2038	+ 118%	1825	+ 117%
28.2	2693	+ 114%	2531	+ 129%	2273	+ 143%	2032	+ 152%

Table 5. TP PI rheology results

hBN Weight % Temperature	390	Δ	400	Δ	410	Δ
0	1472		1119		878	
14.5	2423	+ 165%	1946	+ 174%	1623	+ 185%
17.8	3647	+ 248%	2968	+ 265%	2492	+ 284%
23.6	4282	+ 291%	3449	+ 308%	2933	+ 334%

4. CONCLUSIONS

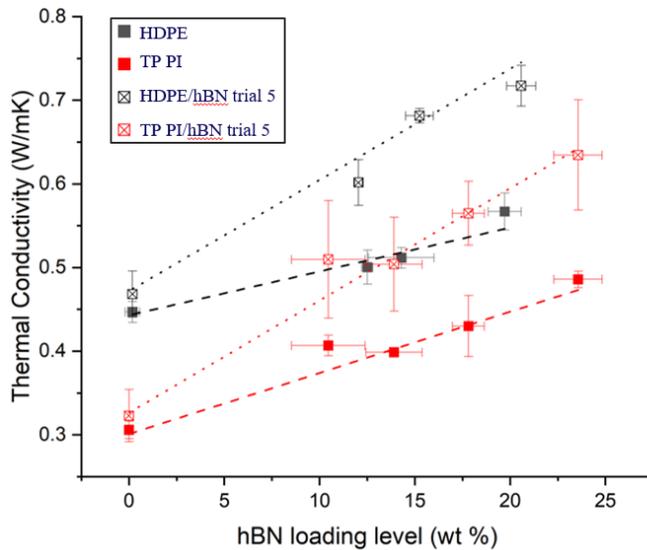


Figure 7. Room temperature thermal conductivity (κ) analyses of post-processed HDPE and TP PI composites with PT180 hBN. Thermal conductivity measured in the through-plane (\ddagger) direction.

Thermoplastic polyimides are a promising polymer matrix candidate, with good high-temperature performance. It was demonstrated that introduction of thermally conductive hBN platelets into TP PI resulted in increases in κ as high as +58%. However, it was also seen that these concentrations resulted in significant increases in brittleness and viscosity, with hBN concentrations above 30 wt% resulting in composites too brittle for the envisioned application and viscosity increases as high as +300%. Therefore, post-processing techniques are currently being pursued which could be readily translated to commercially relevant manufacturing processes with early results suggesting achievement of up to 2x impacts on composite $\ddagger \kappa$ (**Figure 7**).

4.1 Notes

*Official contribution of the National Aeronautics and Space Administration; not subject to copyright in the United States. Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

4.2 Acknowledgements

The authors would like to acknowledge funding support from NASA's Advanced Air Transport Technologies (AATT) and Transformational Tools and Technologies (TTT) projects in the Aeronautics Research Mission Directorate and the Biological and Physical Sciences Division. The authors would also like to acknowledge Drs. Andrew Woodworth and Maricela Lizcano for their technical expertise.

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