

# FABRICATION OF EXTRUDED POLYPHENYLSULFONE – BORON NITRIDE COMPOSITE TAPES

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## ABSTRACT

Polyphenylsulfone (PPSU) is a high-temperature, chemically resistant thermoplastic with high impact resistance that is often used in interior aircraft cabin components, medical devices, and membranes. The aforementioned properties have led to interest investigating PPSU's compatibility with hexagonal boron nitride (hBN) platelets as a thermally conductive, electrical composite insulator for high power-density electric machines. Preliminary trials extruding PPSU-hBN composite tapes showed promising dielectric properties and higher thermal conductivity as a function of hBN concentration compared to their neat analog. On the other hand, only few studies have reported on the extrusion process and resulting thermo-mechanical properties for PPSU and its composites made with chopped fiber reinforcement or fillers, none of which containing boron nitride filler. Prospects may exist for this type of material to be incorporated into extrusion-based additive manufacturing techniques to print other composites bearing unique properties useful for aerospace. Loading levels with up to approximately 23 wt% were achieved using micro-size BN platelets without observing any significant affects to PPSU's glass-transition temperature. This work includes a description of the rheological properties of PPSU, the extrusion parameters for mixing and compounding the PPSU-hBN composite tapes, and the thermal and thermo-mechanical properties of PPSU-hBN composites.

Keywords: polyphenylsulfone, boron nitride, extrusion, high temperature thermoplastics, thermoplastic composites

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## 1. INTRODUCTION

Thermally conductive polymers are receiving increasing interest for their ability to dissipate heat in compact, power-dense electronic devices. In addition, the aviation industry is making progress toward the electrification of aircraft, a change that will require high electrical power density systems and hence, electrical subcomponents to release a significant amount of heat, as well as withstand other associated increases in electrical and mechanical stress [1]. For this reason, significant effort has gone into investigating novel high-temperature, thermally conductive polymer insulation for thermal management in electrified aircraft.

Boron nitride (BN) is believed to be an ideal dielectric filler for high power density electric motors, because it is electrically insulating, non-abrasive, and it has high in-plane thermal conductivity. Dielectric and thermally conductive properties of polyimide-BN and epoxy-BN have been reported [2-4] and it was shown that the thermal conductivity was significantly improved over that of the virgin polymer. Boron nitride has also been reported to have radiation shielding properties, which could make it a prospective filler to create structural radiation-resistant polymer composites for aerospace [5]. Literature has often reported solvent usage for thin membrane and composite film fabrication to facilitate casting and the incorporation and dispersion of filler into the matrix [6, 7]. Solvent usage is often considered a disadvantage from the standpoint of health and manufacturing scalability. Alternatively, extruding thermoplastic composite films could be a preferable processing technique over solvent film casting, but only a few studies have discussed processing parameters and properties resulting from extruding high temperature thermoplastics with boron nitride platelets [8, 9].

Polyphenylsulfone (PPSU) is a polymer often used for membrane applications because it is chemically resistant, has high toughness, and a high thermal stability and glass-transition temperature ( $T_g$ ). The aforementioned properties led to interest in investigating PPSU with hexagonal BN (hBN) as a thermally conductive composite insulator for high power density electric motors. Preliminary dielectric and thermal conductivity data on extruded PPSU-hBN composite films were promising, but very little information was reported about the processing conditions and thermo-mechanical properties [10]. There is also very few literature on PPSU composite extrusion with other fillers and reinforcement [11]. The objective of this study was to establish an extrusion method for processing PPSU thermoplastic composites tapes with hBN platelets. The rheological, morphological, thermal, and thermo-mechanical properties will be discussed.

## 2. EXPERIMENTATION

### 2.1 Materials and Fabrication

#### 2.1.1 Materials

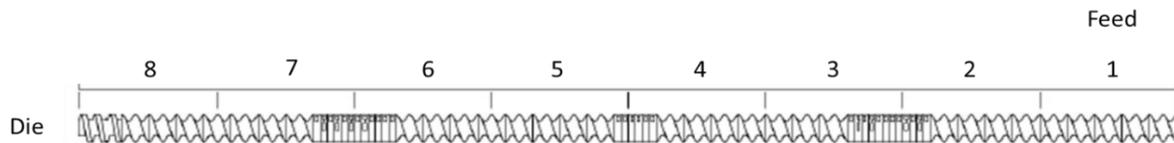
Radel® R-5500 polyphenylsulfone pellets of around 2.5 – 3.0 mm were processed in their as-received form. Prior to extrusion, PPSU pellets were oven-dried at 170 °C for 24 hours and then stored in a cool, dry location prior to use. Momentive PT180 hexagonal boron nitride platelets (mean particle size: 6-9  $\mu\text{m}$ ) were used as the thermally conductive filler [12]. The hBN fillers were used in their as-received form.

### 2.1.2 Composite Fabrication by Twin-Screw Extrusion

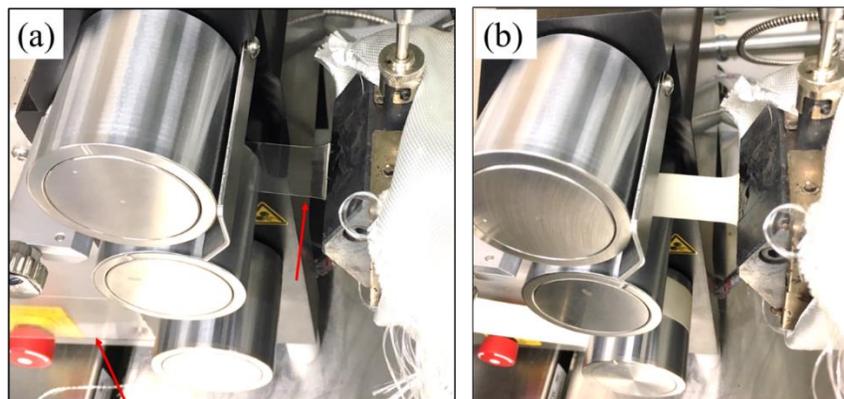
Twin-screw extrusion experiments were carried out using a co-rotating 11 mm twin-screw extruder (L/D=40). The extruder was equipped with a sheet die and a water-cooled sheet take-off accessory. Volumetric twin-screw and single screw feeders were used to dispense the hBN powder and PPSU pellets, respectively, at zone 1 of the barrel at a specified rate. Feeder calibration was performed by setting a feed rate and measuring the mass of material fed during a 60s time interval. Calibrations were performed in triplicate. Extruded tapes were  $0.3 \pm 0.1$  mm thick. Extruder heating zones were set to the temperatures reflected in Table 1. Actual temperatures were slightly deflated in zones 2 and 3 due to the integrated water-cooling function that was located at the feeding point of zone 1. The screw design used for all experiments is illustrated in Figure 1. The screw speed was maintained at 80 rpm. Figure 2 shows the (a) transparent neat PPSU and (b) PPSU-hBN composite tapes exiting the die. Fiberglass was wrapped around the sheet die to maintain die temperature and resultantly, dimensional stability, of the extrudate. The extruded tapes were tensioned slightly as the material was carried from the die onto the sheet take-up wheel.

**Table 1.** Hopper-to-die temperatures for extruded polyphenylsulfone (PPSU) and PPSU-boron nitride composite tapes. No heating occurs at zone 1.

Zone #	Die	8	7	6	5	4	3	2
Set (°C)	350	350	350	370	370	380	380	380
Actual (°C)	350	350	350	370	370	380	359	278



**Figure 1.** Screw configuration used to extrude PPSU and PPSU-hBN composites (Figure was adapted from [13]).



**Figure 2.** (a) Neat PPSU and (b) PPSU-hBN composite tapes exiting the sheet die. The air knife is attached to the top water-chilled roller. Red arrows point to the unfilled, transparent PPSU film.

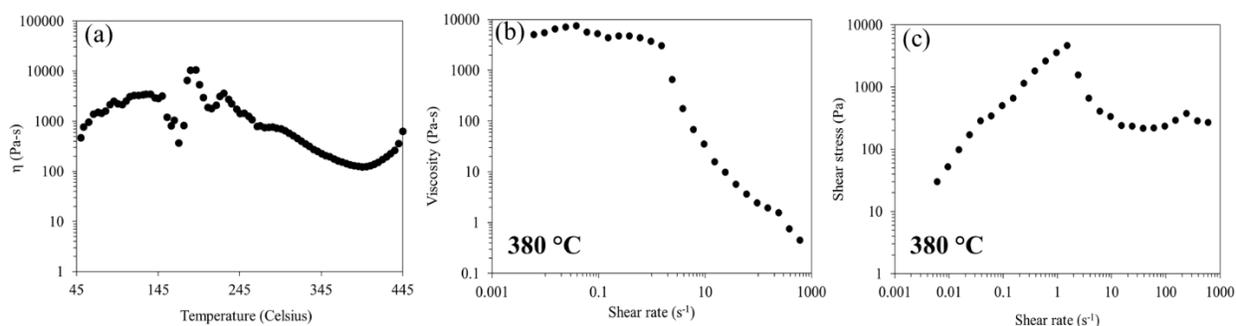
## 2.2 Characterization

The starting materials and extruded films were characterized to understand the rheological behavior of PPSU and the influence of filler on the morphology, thermal stability, and thermo-mechanical properties of PPSU-hBN composites. A field emission scanning electron microscope was used to examine extruded composites. The microscope was operated at an acceleration voltage of 6 kV. Samples were coated with platinum prior to imaging. Images of the cross-sections were taken by cryo-fracturing the specimens. The rheological properties of the PPSU pellets were characterized using a parallel plate ARES rheometer. A temperature ramp was carried out from ambient temperature to 445 °C to determine the viscosity as a function of temperature. Steady state shear experiments were carried out at 5% strain at ~380 °C. Thermo-gravimetric Analysis (TGA) was carried out to determine the effect of hBN loading on the decomposition profile and to confirm the hBN loading level in the extruded composites. Although calibration was done to a high degree of accuracy, process related events often led to loading levels that deviated from the target. Specimens were cut directly from the extruded films and placed onto aluminum TGA pans. Analysis was performed using a 10 °C/min ramp from room temperature to 900 °C in an air environment. The hBN loading level was determined by the char yield at 900 °C; analyses were performed on randomly selected specimens from the bulk roll of tapes. Dynamic Mechanical Analysis (DMA) was carried out in multi-frequency strain mode. A tensile fixture was used for DMA experiments where specimens were ramped from ambient temperature to 300 °C at a ramp rate of 5 °C/min. Sample dimensions were kept consistent at dimensions of approximately 20.0 mm (l) x 6.0 mm (w) x 0.3 mm (t).

## 3. RESULTS

### 3.1 Rheological Properties of Polyphenylsulfone

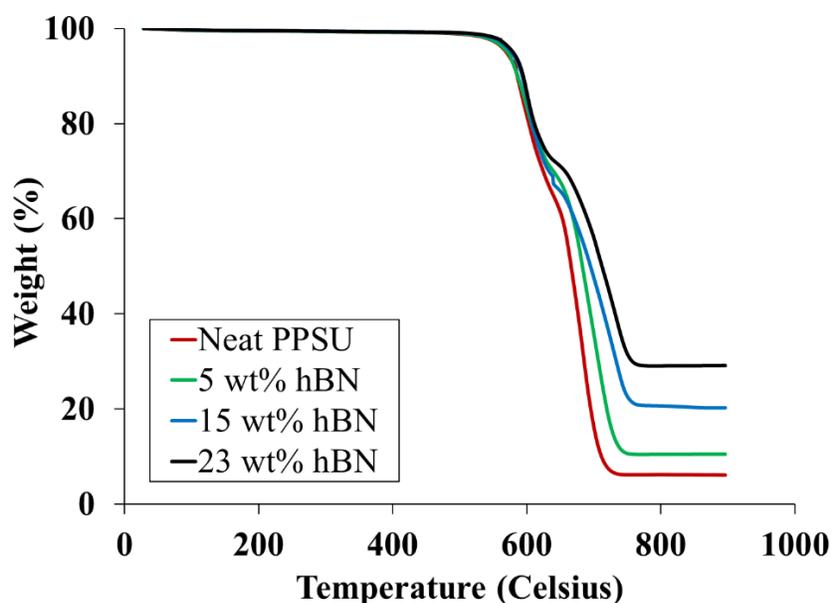
Polyphenylsulfone pellets were introduced to the rheometer parallel plates at room temperature. Figure 3(a) shows that the viscosity fluctuated between ~145 °C and ~225 °C, which was a reflection of PPSU pellet breakage, shearing, and heating taking place simultaneously as the polymer became more fluid. As the temperature further increased, the low melt viscosity temperature of PPSU was observed at around 400 °C. The rheological behavior of PPSU is shown in the steady state shear experiments in Figures 3(b) and (c). The tests were carried out at 380 °C, which was selected because this was the predominant temperature used at the mixing zones during the extrusion experiments. Figure 3(b) showed a Newtonian to non-Newtonian transition with increasing shear rates, which is typical behavior of thermoplastics. Figure 3(c) revealed that the shear stress of neat PPSU peaked at a shear rate of  $1\text{s}^{-1}$  prior to decreasing in the shear-thinning zone. Rheology data was not obtained for PPSU-hBN composites due to the shearing and mixing action of the rheometer not being representative of the composites that are compounded and mixed in the twin-screw extruder.



**Figure 3.** Rheological properties of neat polyphenylsulfone. Steady state shear experiments in (b) and (c) were carried out at 380 °C.

### 3.2 Thermal stability of Extruded PPSU and PPSU-hBN Composites

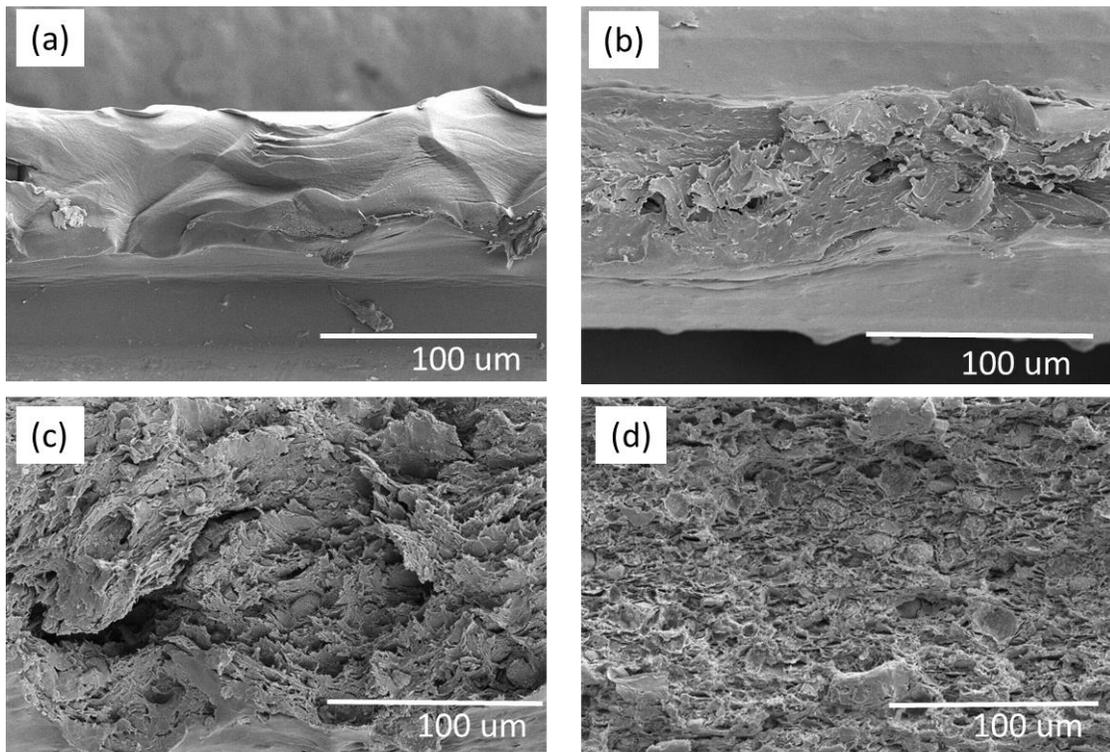
The effect of hBN platelet loading on the thermal stability of PPSU in air was observed in Figure 4. The residual char yield at ~900 °C was used to determine the hBN loading levels, which was ~5 wt%, ~15 wt%, and 23 wt%. A two-step decomposition profile was observed from the TGA curves. Figure 4 showed that introducing up to 23 wt% hBN micro-platelets to PPSU led to very little change at the first onset decomposition temperature ( $T_{d1}$ ), which was near ~570 °C. The mass loss corresponding to  $T_{d1}$  was attributed to decomposition of the sulfonated functional groups [6]. A second onset decomposition temperature,  $T_{d2}$ , appeared near 660 °C, which was more than likely attributed scission of the hydrocarbons in the main-chain of PPSU. The second  $T_d$  was more affected by hBN fillers, in which the  $T_{d2}$  was observed to increase to ~689 °C at the highest filler loading of 23 wt% hBN.



**Figure 4.** Effect of hBN filler on the thermal stability of extruded PPSU films

### 3.3 Morphology of Extruded PPSU and PPSU-hBN Composites

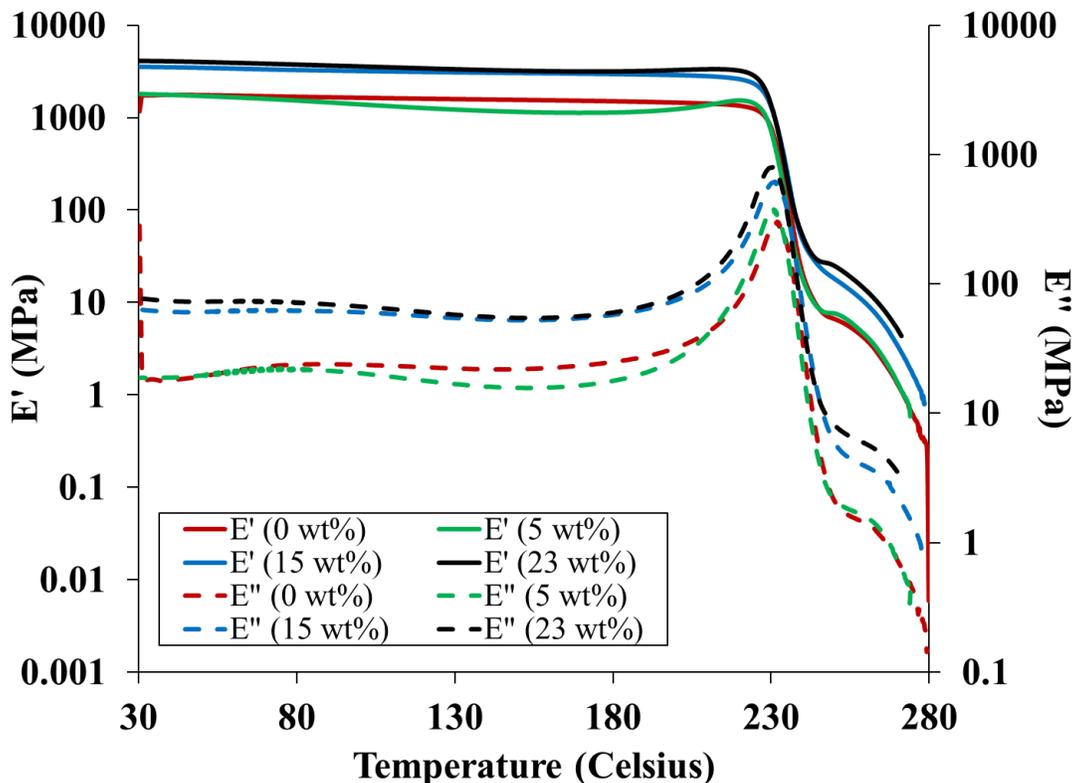
Dispersion of the hBN particles was examined by imaging the cross-section of the PPSU-hBN composites. The SEM micrograph in Figure 5(a) showed a consolidated cross-section for the neat PPSU. The jagged appearance of the cross-section was caused from difficulty obtaining a clean fracture surface when attempting to break the tough PPSU films after liquid N<sub>2</sub> submersion. Figure 5(b) shows the cross-section of the PPSU-hBN composite tape with ~5 wt% hBN loading. Mixing-related defects were observed mostly at the sites of the resin-hBN interfaces. The presence of gaps observed at the hBN-polymer interfaces was more frequent as shown in Figures 5(c) and (d), which was a result of the increased filler loading. Air gaps at the polymer-filler interfaces would increase phonon scattering, thereby adversely affecting thermal conductivity. Evidence of hBN agglomeration was observed in some areas of the micrographs in Figure 5(c) and (d). Using a blend of exfoliated nanoplatelets with micro-sized platelets may be a remedy for minimizing the void spaces within the matrix. An approach to reducing agglomerate size includes modifying the screw configuration to enhance dispersive mixing of the micro-hBN platelets in the matrix. Although the amount of mixing-induced defects increased with higher filler loadings, the hBN platelets appeared to be distributed homogeneously throughout the matrix.



**Figure 5.** Scanning electron micrographs of the cross-section of (a) neat PPSU at x500, working distance (WD) 9.9 mm; (b) PPSU with ~5 wt% hBN at x500, WD 10.1mm (c) PPSU with ~15 wt% at x500, WD 10.2mm and (d) ~23 wt% hBN loading in PPSU at x500, WD 12.0mm

### 3.4 Effect of hBN Concentration on the thermo-mechanical properties of PPSU films

Dynamic mechanical analysis was used to characterize the thermo-mechanical properties of the PPSU and PPSU-hBN composite tapes as a function of hBN concentration. The storage modulus ( $E'$ ) and loss modulus ( $E''$ ) curves are shown in Figure 6. Figure 6 showed that the neat PPSU film had an  $E'$  of approximately 1.7 GPa. At 5 wt % hBN loading, the  $E'$  was almost unchanged, but as the hBN loading increased to 15 wt% and 23 wt%, the  $E'$  increased to approximately 3.6 and 4.1 GPa, respectively. The PPSU-hBN composite films were still very flexible at 23 wt% loading using micro-sized hBN platelets. The  $T_g$  was determined by locating the temperature at which the  $E''$  peak maximum occurs, and was observed to be approximately 230 °C. The hBN platelets did not appear to significantly affect the  $T_g$ , which can be expected due to the absence of surface functional groups on the particles that would increase particle-polymer interactions. On the other hand, the area and height of the  $E''$  curves increased with higher hBN concentrations, which was more than likely attributed to the increased friction taking place between the hBN platelets and polymer chains as more segmental motion occurred as temperatures approached the alpha transition temperature.



**Figure 6.** Effect of hBN filler loading on the storage modulus ( $E'$ ) and loss modulus ( $E''$ ) of PPSU-hBN composite tapes. The solid lines represent  $E'$  and  $E''$  is represented by hashed lines.

## 4. CONCLUSIONS

The process to extrude and characterize PPSU composite tapes with up to 23 wt% micro-sized hBN platelets was discussed. Scanning electron microscopy images showed the orientation of micro-sized hBN platelets along the extrusion plane. The amount of air gaps between hBN agglomerates and PPSU at the polymer-filler interface increased as the hBN concentration increased. Thermo-gravimetric analysis revealed the two-step decomposition profile in PPSU-hBN where the sulfonated groups decomposed near ~570 °C in air and was independent of hBN loading. Main chain decomposition took place at ~662 °C for neat PPSU and increased to ~689 °C with 23 wt% hBN loading. The  $E'$  for neat PPSU was determined to be ~1.7 GPa, which increased to ~4.1 GPa at the highest hBN loading. The  $T_g$  of ~230 °C remained unchanged with hBN filler addition. Efforts are underway to further optimize the extrusion process to reduce both the hBN agglomerate and interface sizes, which should correspond to an enhancement in thermal conductivity.

## 5. REFERENCES

1. “Commercial Aircraft Propulsion and Energy Systems Research: Reducing Global Carbon Emissions.” National Academies of Sciences, Engineering and Medicine. Washington, DC: The National Academies Press, 2016. doi:10.17726/23490
2. Diaham, S., Saysouk, F.ç., Locatelli, M.-L., Belkerk, B., Scudeller, Y., Chiriac, R., Toche, F.ç. and Salles, V. “Thermal conductivity of polyimide/boron nitride nanocomposite films.” *J. Appl. Polym. Sci.*, 132 (2015): 42461, doi: [10.1002/app.42461](https://doi.org/10.1002/app.42461)
3. Tanimoto, M., Yamagata, T., Miyata, K., Ando, S. “Anisotropic thermal diffusivity of hexagonal boron nitride-filled polyimide films: Effects of filler particle size, aggregation, orientation, and polymer chain rigidity.” *ACS Appl. Mater. Interfaces* 5(10) (2013): 4374-4382.
4. Donnay, M., Tzavalas, S., Logakis, E. “Boron nitride filled epoxy with improved thermal conductivity and breakdown strength.” *Compos. Sci. Technol* 110 (2015): 152-158.
5. Thibeault, S. A., Fay, C. C., Lowther, S. E., Earle, K. D., Sauti, G., Kang, J. H., Park, C., McMullen, A. M. “Radiation Shielding Materials Containing Hydrogen, Boron, and Nitrogen: Systematic Computational and Experimental Study.” HQ-E-DAA-TN33851, 2012.
6. Arockiasamy, D. L., Alam, J. “Carbon nanotubes-blended poly(phenylene sulfone) membranes for ultrafiltration applications.” 3 (2013): 93-103, doi:10.1007/s13201-012-0063-0
7. Kiani, S., Mousavi, S. M., Saljoughi, E., Shahtahmassebi, N. “Preparation and characterization of modified polyphenylsulfone membranes with hydrophilic property for filtration of aqueous media.” *Polymers Advanced Technologies* 29 (2018): 1632-1648, doi:10.1002/pat.4268
8. Ng, H. S., Lu, X. “Thermal conductivity of boron nitride-filled thermoplastics: Effect of filler characteristics and composite processing conditions.” *Polymer Composites* (2005): 778-790.
9. Zhang, X., Zhang, J., Xia, L., Li, C., Wang, J., Xu, F., Zhang, X., Wu, H., Guo, S. “Simple and Consecutive Melt Extrusion Method to Fabricate Thermally Conductive Composites with

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*Highly Oriented Boron Nitrides.*” *ACS Appl. Mater. Interfaces* 9 (2017): 22977-22984, doi: 10.10121/acsami.7b05866

10. Williams, T., Nguyen, B., Fuchs, W. *Polyphenylsulfone-hBN Composite Insulation*. Valencia, Spain : IEEE, 2020. IEEE 2020 International Conference on Dielectrics. pp. 541-545.
11. McGarrigle, M. W., McIlhagger, A., Harkin-Jones, E., Archer, E. *Effect of extrusion parameters and nanofillers on mechanical properties of PPSU tufting yarns*. Dresden, 2019. AIP Conference Proceedings 2055. p. 060003, doi:10.1063/1.5084835
12. PolarTherm\* Boron Nitride Powder: PT140, PT160 and PT180. [Online] [https://www.momentive.com/docs/default-source/productdocuments/boron-nitride-powder-polartherm-and-polartherm-ptx-additives/polartherm-bn-powder-grades-pt140-pt160-pt180.pdf?sfvrsn=c8a89c21\\_18](https://www.momentive.com/docs/default-source/productdocuments/boron-nitride-powder-polartherm-and-polartherm-ptx-additives/polartherm-bn-powder-grades-pt140-pt160-pt180.pdf?sfvrsn=c8a89c21_18) (Accessed December 7, 2020)
13. *Process 11 Twin Screw Extruder Manual*. 2013. Doc. No. 042-3687.