Journal of Mines, Metals and Fuels, *71(12): 2814-2820; 2023. DOI: 10.18311/jmmf/2023/41615*

Print ISSN : 0022-2755

Journal of Mines, Metals and Fuels

Contents available at: *www.informaticsjournals.com/index.php/jmmf*

Hexagonal Boron Nitride Nanoplatelets Filled Polyphenylene Sulphide Nanocomposites: Influence on Thermal and Dielectric Properties

Pankaj Tambe[1]*, Ambuj Sharma[1], Hrushikesh Kulkarni[2], Biswajit Panda[3] and Mayank Pandey[4]

[1]School of Mechanical Engineering VIT-AP University, Amarvati – 522237, Andhra Pradesh, India; pankaj.tambe@vitap.ac.in

[2]School of Mechatronics Engineering, Symbiosis Skill and Professional University, Pune – 412101, Maharashtra, India

[3]Department of Applied Science Mathematics and Humanities, Pillai College of Engineering, Navi Mumbai – 410206, Maharashtra, India

[4]Department of Electronics, Kristu Jayanti College, Bengaluru – 560077, Karnataka, India

Abstract

The Hexagonal Boron Nitride (hBN) nanoplatelets are synthesized using a wet chemical method. X-Ray Diffraction (XRD) shows the hBN nanoplatelets exfoliates along the (002) plane. Transmission Electron Microscope (TEM) observation shows the exfoliated hBN nanoplatelets. The hBN nanoplatelets and polyphenylene suulfiude (PPS) physical mixture are solvent processed using ethyl alcohol. It involves two step processing with the first step of ultrasonic treatment of hBN nanoplatelet in ethyl alcohol followed by mixing it with PPS powder and further sonication. This mixed powder of PPS and hBN nanoplatelets are hot pressed using a compression moulding machine. With more addition of hBN nanoplatelets in PPS matrix shows the enhancement in dielectric constant. In addition, the dispersion of hBN nanoplatelets in the PPS matrix increases the crystallinity and thermal stability.

Keywords: Hexagonal Boron Nitride, Polyphenylene Sulphide, Thermal Stability, Transmission Electron Microscope, X-Ray Diffraction.

1.0 Introduction

The hBN nanosheets and nanoplatelets were of commercial importance because of its high thermal conductivity[1-3]. The hBN nanosheets were synthesized using various methods. The hBN nanosheets and nanoplatelets are mixed in polymer matrix to obtain advanced functional nanocomposites. Saha *et al.*[4] incorporated the hBN nanoplatelets in the polymer phase to improve the flexural properties. While Kulkarni *et al.*[5] incorporated the hBN nanosheets into the polymer phase which shows the reduction in dielectric constant. For details regarding the developments of the hBN nanosheets filled polymer nanocomposites, the review articles related to this area can be referred[6]. Engineering thermoplastics are of great importance. The engineering thermoplastic like Poly (Phenylene Sulfide) (PPS) is suitable for the electronics packaging applications. The PPS has good thermal stability with compressive strength[7-9]. Kim *et al.*[10] mixed hBN nanosheets with PPS by melt processing to improve the thermal conductivity. Since, the PPS/hBN nanocomposites are attractive in terms of applications. Thus in this work, the dielectric properties and thermal behaviour of PPS/hBN nanoplatelets nanocomposites were investigated.

**Author for correspondence*

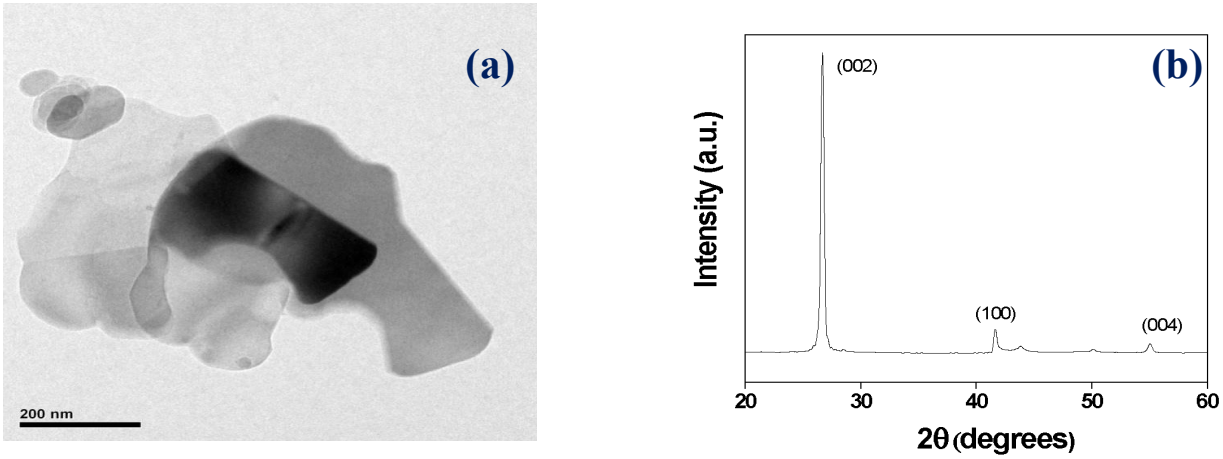

Figure 1. (a) TEM and (b) XRD of hBN nanoplatelets.

2.0 Experimental

2.1 Materials

The material used in this work is as follows. PPS from Sigma Aldrich (Mn – 10000), hBN powder of 309 mesh,, Momentive Performance Materials, India; potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), ethyl alcohol obtained from SD Fine Chemicals, India of analytical reagent grade.

2.2 Processing of PPS/hBN Nanoplatelets Nanocomposites

The synthesis method of hBN nanoplatelets follows the protocol established earlier[4]. The 6 gm of micron size hBN powder in put inside the 150 ml of sulfuric acid (H_2SO_4) with constant stirring. Thereafter, the addition of 1.5 gm of potassium permanganate ($KMnO_4$) was added slowly. The reaction was continued for 12 hours followed by addition of 3% hydrogen peroxide (H_2O_2). The obtained hBN nanoplatelets were washed several times followed by vacuum drying.

PPS/hBN nanoplatelets nanocomposite was processed by mixture of graphene and PPS in ethyl alcohol by probe sonication. The hBN nanoplatelets were sonicated first followed by PPS addition and further sonication. The probe sonication was done for 60 minutes. The sonicated solution was dried in a vacuum oven at 70°C to obtain PPS/hBN nanoplatelets powder. The vacuum dried powder was compression moulded at 320°C for 30 minutes to prepare the sample specimens of 20 mm diameter and 3 mm thickness.

2.3 Characterization of PPS/hBN Nanoplatelets Nanocomposites

The characterization methods used in this work is as follows. TEM of Philips make CM-200; Differential scanning calorimeter (DSC, DSC-60 Plus of Shimadzu with operating condition of 50-260°C @ 5°C/min); Thermogravimetric analysis (TGA, TGA- 50 of Shimadzu with operating condition of 40-260°C @ 10°C/min); Scanning electron microscope (SEM, TESCAN (BEGA-3)), X-ray diffraction (XRD, BRUKER XRD of D8 Advanced); AC Impedance Spectroscopy of Newton's 4th Impedance Analyser.

3.0 Results and Discussion

3.1 hBN Nanoplatelets Characterization

The hBN nanoplatelets have been synthesized using chemical method. The method used for synthesis was adopted from the literature[4]. In this protocol, the exfoliation obtained is more due to double the concentration of MnO_2 nanoparticles intercalated in between the layers of hBN nanosheets. The synthesized hBN nanoplatelets were initially observed TEM. The TEM image shown in Figure 1a revealed a surface morphology of hBN nanoplatelets.

The hBN nanoplatelets show layered sheet structures with smooth surfaces and edges. In Figure 1a, multi-layered structure of hBN nanoplatelets is observed. The width of hBN nanoplatelets is found in the range of 200 nm to 800 nm. Assembly of hBN nanoplatelets are also noticed resulting in different levels of transparencies. The different extent of transparency in the morphology indicates the difference in amount of stacking of hBN nanoplatelets. The darkest areas in the morphology indicate the thick stacking of several layers hBN nanoplatelets, while the comparative transparent areas in the morphology indicate thinner films of few layers of hBN nanoplatelets. Further, the synthesized hBN nanoplatelets were characterized using XRD. Figure 1b represents the XRD pattern of hBN nanoplatelets which shows the highly-ordered crystalline structure of hBN nanoplatelets. From the Figure 1b, it is clear that hBN nanoplatelets shows many diffraction peaks cantered at 26.5, 41.6, 44.0, 50.1 and 55.2 which is associated to (002), (100), (101), (102) and (004) planes, respectively. More intense and sharp peak detected at 26.6 corresponding to the plane (002) is associated to the crystallographic plane of the hBN crystal structure[11]. This observation further confirms the hexagonal structure of boron nitride.

3.2 Morphology of PPS/hBN Nanplatelets Pressed Powder

The hBN nanoplatelets dispersion with PPS powder has to be characterized in order to correlate with the thermal and dielectric properties. The hBN nanoplatelets were mixed with PPS powder with solvent method. The dried mixture of hBN nanoplatelets and PPS was cold pressed at 15 MPa and break to observe the fracture surface. To analyse the influence of hBN nanoplatelets on the phase morphology of PPS/hBN nanocomposites, SEM was carried out and represented in Figure 2. Three samples with varying concentration of hBN nanoplatelets of 1, 3 and 4 wt.% incorporated in PPS matrix was observed. A rough surface is observed (Figure 2a) on dispersion of 1

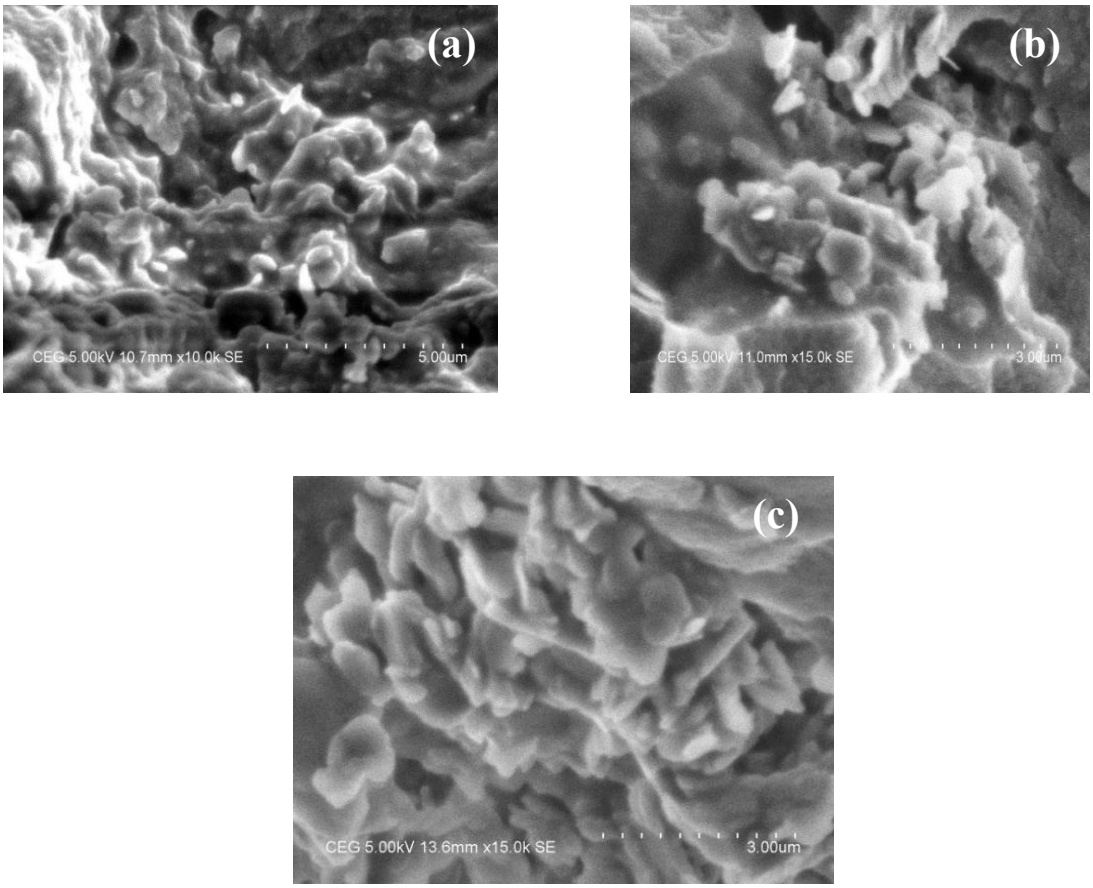

Figure 2. SEM images of (a) PSS+1 wt.% hBN (b) PSS + 3 wt.% hBN(c) PSS + 4 wt.% hBN nanoplatelets.

wt% of hBN nanoplatelets in PPS phase. The 3 wt.% of hBN nanoplatelets in PPS phase reveals the more density of hBN nanoplatelets as encircled in Figure 2b. On further addition of to 4 wt.% hBN nanoplatelets in PPS phase exhibit the agglomerates of hBN nanoplatelets as shown in Figure 2c.

3.3 Thermal Properties of PPS/hBN Nanplatelets Nanocomposites

The incorporation of hard nanoparticles like hBN nanoplatelets can influence the crystallization behaviour of PPS matrix. In this aspect, differential scanning calorimetry (DSC) was done over the PPS/hBN nanoplatelets nanocomposites. The melting endotherm of pure PPS and PPS/hBN nanoplatelets nanocomposites are represented in Figure 3a. All the samples of neat PPS and PPS/hBN nanoplatelets nanocomposites show a single melting peak in the DSC scan. The melting temperature (T_m) of PPS is centred on 283.7°C. A decrease in T_m is noticed for all PPS/hBN nanoplatelets nanocomposites samples. It was well known that the T_m of semi-crystalline polymer depends on the lamellae thickness[12]. In addition, the interaction energy between the lamellae and amorphous chain also influences the T_m[12]. From the literature, it was observed that the lamellae thickness decreases with incorporation of fillers in the polymer matrices[13,14]. It is expected that the incorporation of hBN nanoplatelets reduces the thickness of lamellae, which is the reason for a decrease in T_m of PPS/ hBN nanoplatelets nanocomposites. From the melting endotherm, the ratio of normalized enthalpy to 100% crystalline melting enthalpy (76.5J/g) was used to calculate the crystallinity[15]. Figure 3b shows the plot of % crystallinity of PPS/hBN nanoplatelets nanocomposites as a function of hBN nanoplatelets concentration. It is clear form the plot of Figure 3b that the increase in % crystallinity of PPS with an incorporation of hBN nanoplatelets exhibiting the linear relationship.

Thermogravimetric Analysis (TGA) was done over the pure PPS and PPS/hBN nanoplatelets nanocomposites to study thermal stability. Figure 4 represents the weight loss profile for PPS with a variation of temperature for neat PPS and PPS/hBN nanoplatelets nanocomposites with varying concentration of hBN nanoplatelets from 1 wt.% to 4 wt.%. All the composition shows a single step degradation over the entire temperature cycle for pure PPS and PPS/hBN nanoplatelets nanocomposites as shown in Figure 4a. From Figure 4b, it is clear that the gradual addition of hBN nanoplatelets shift the TG cures which indicate the increase in thermal stability of PPS. The highest thermal stability is seen in 4 wt.% concentration of hBN nanoplatelets in PPS matrix. It was clear from the SEM image that the hBN nanoplatelets were closed to each other, which can form a char and results in improvement in thermal stability by not allowing the diffusion of gases at high temperature[8].

The maximum degradation temperature (T_{mg}) can be found out by taking the differential of TG curves. Figure 5 shows the Differential Thermogravimetric (DTG) curves for pure PPS and PPS/hBN nanoplatelets nanocomposites with varying concentration of hBN nanoplatelets from 1 wt.% to 4 wt.%. From the DTG curve only one main

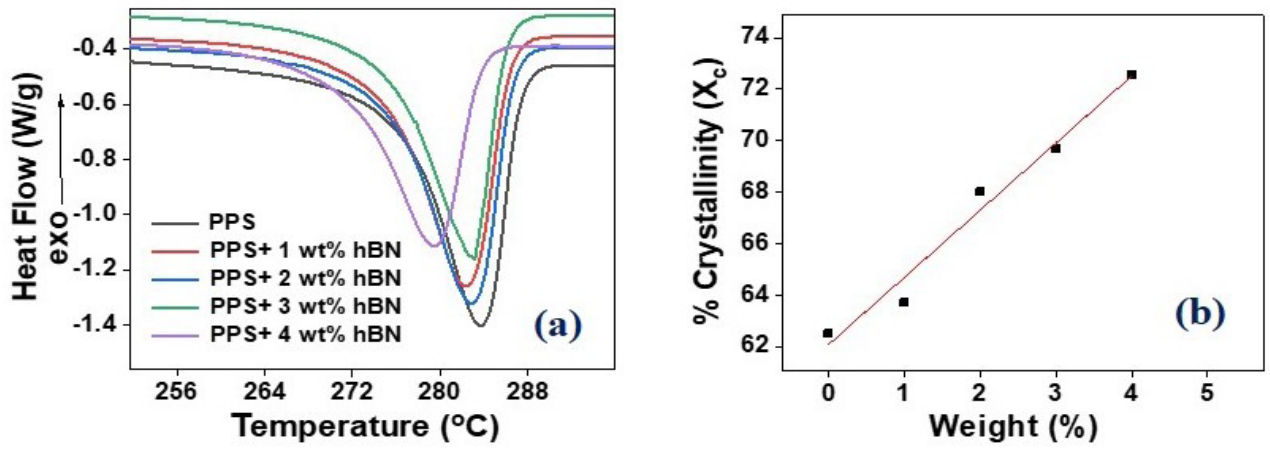

Figure 3. (a) Melting endotherms (b) % Crystallinity of PPS and hBN nanoplatelets filled PPS nanocomposites.

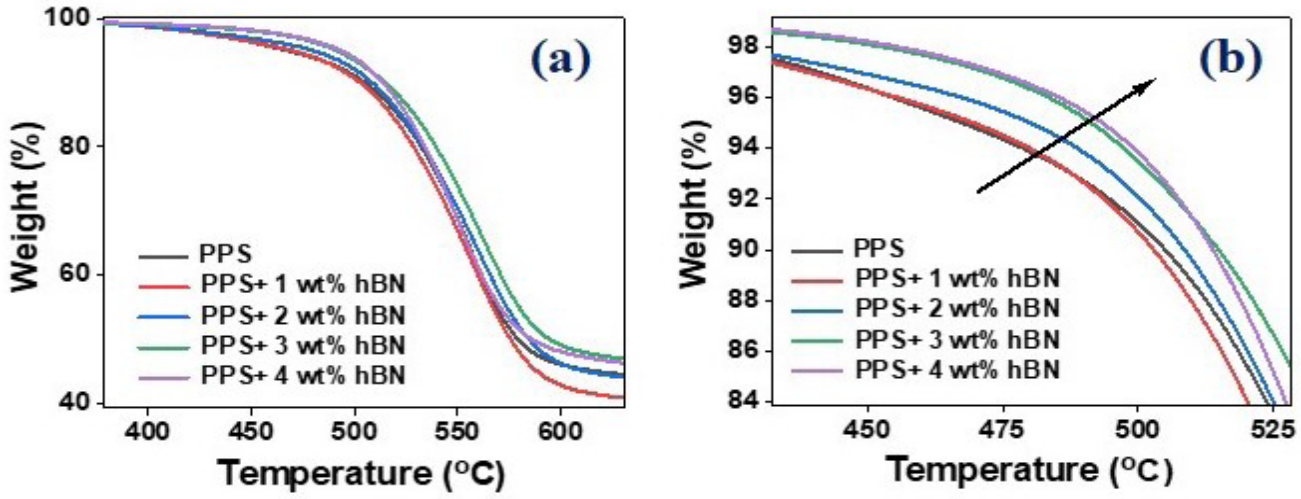

Figure 4. TG curves of PPS and hBN nanoplatelets filled PPS nanocomposites.

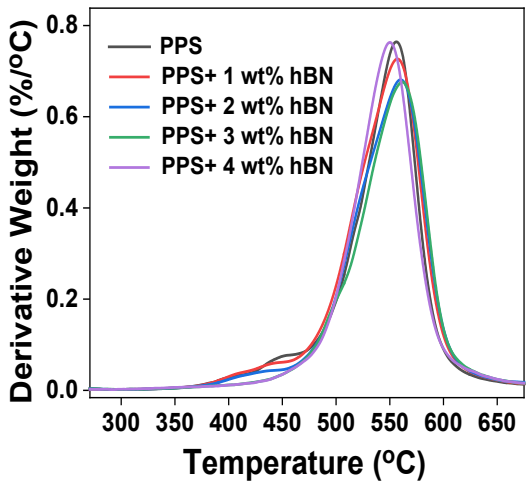

Figure 5. DTG curves of hBN nanoplatelets filled PPS nanocomposites.

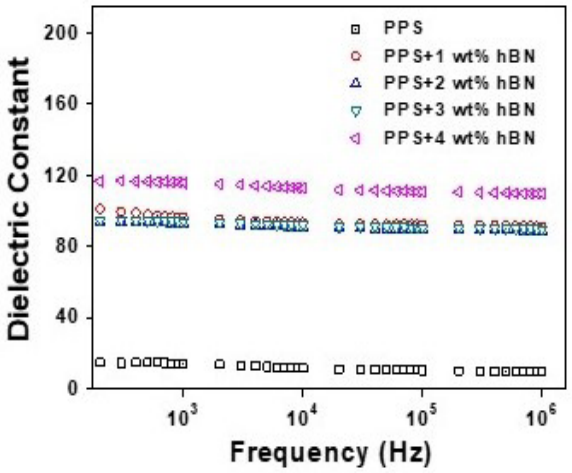

Figure 6. Dielectric constant of hBN filled PPS nanocomposites.

mass loss step is observed between 450°C and 650°Cfor all the compositions. The T_{mg} of the hBN nanoplatelets up to 3 wt.% in PPS matrix shows the increase as compared to pure PPS. While the hBN nanoplatelets of 4 wt.% in PPS matrix shows the decrease as compared to pure PPS due to the network of highly thermally conducting hBN nanoplatelets network facilitates early thermal degradation.

3.4 Electrical Properties of PPS/hBN Nanplatelets Nanocomposites

The AC impedance spectroscopy was carried out over the pure PPS and PPS/hBN nanoplatelets nanocomposites with varying concentration of hBN nanoplatelets from 1 wt.% to 4 wt.%. The influence of dielectric constant vs. frequency pure PPS and PPS/hBN nanoplatelets nanocomposites with varying concentration of hBN nanoplatelets from 1 wt.% to 4 wt.% is presented in Figure 6. The dispersion of 1 wt.% of hBN nanoplatelets in PPS matrix increases the dielectric constant significantly. The main reason is uniform dispersion of hBN nanoplatelets in PPS matrix. The interfacial polarization between the PPS matrix phase and the interfacial polarization between the matrix phase and hBN nanoplatelets increases the dielectric constant[16,17]. At higher concentration of hBN

nanoplatelets in PPS phase do not increase the dielectric constant significantly. While addition of 4 wt.% of hBN nanoplatelets in PPS matrix suggest highest enhancement in dielectric constant. It is important to note that composites with high dielectric constant values would be beneficial for capacitors applications.

4.0 Conclusion

In the present work wet chemical methods were used successfully utilized to synthesise hBN nanoplatelets. XRD studies confirm the hexagonal structure and exfoliation of hBN along the (002) plane. The structure of exfoliated hBN nanoplatelets is further confirmed through TEM analysis. The PPS nanocomposites containing varying concentrations of hBN nanoplatelets were processed by solvent using ethyl alcohol. Two step mixing processes were employed and the mixtures of powder of PPS and hBN nanoplatelets were hot pressed using a compression moulding machine. It was noticed that gradual addition of hBN from 1 wt.% to 4 wt.% in the PPS phase increases the thermal stability of nanocomposites which indicates the better compatibility of the filler with PPS phase. It has been noted that incorporation of hBN nanoplatelets in the PPS matrix increases the crystallinity of PPS phase proportionally. The addition of hBN nanoplatelets in PPS phase shows a positive impact on the dielectric constant values.

5.0 References

1. Coleman JN, Lotya M, O'Neill A, Bergin SD, King PJ, Khan U, *et al.* Two-dimensional nanosheets produced by liquid exfoliation of layered materials. Science. 2011 Feb; 331(6017):568-71. https://doi.org/10.1126/science.1194975 PMid:21292974
2. Du M, Wu Y, Hao X. A facile chemical exfoliation method to obtain large size boron nitride nanosheets. CrystEngComm. 2013 Dec; 15(9):1782-6. https://doi.org/10.1039/c2ce26446c
3. Yu J, Huang X, Wu C, Wu X, Wang G, Jiang P. Interfacial modification of boron nitride nanoplatelets for epoxy composites with improved thermal properties. Polymer. 2012 Jan; 53(2):471-80. https://doi.org/10.1016/j.polymer.2011.12.040
4. Saha M, Tambe P, Pal S, Kubade P, Manivasagam G, Xavior MA, *et al.* Effect of non-ionic surfactant assisted modification of hexagonal boron nitride nanoplatelets on the mechanical and thermal properties of epoxy nanocomposites. Compos Interfaces. 2015 Jun; 22(7):611-27. https://doi.org/10.1080/09276440.2015.1056688
5. Kulkarni HB, Tambe PB, Joshi GM. Influence of surfactant assisted exfoliation of hexagonal boron nitride nanosheets on mechanical, thermal and dielectric properties of epoxy Nanocomposites. Compos Interfaces. 2020 Sep; 27(6):529-50. https://doi.org/10.1080/09276440.2019.1663115
6. Zhang Y, Niu H, Liyun W, Wang N, Xu T, Zhou Z, *et al.* Fabrication of thermally conductive polymer composites based on hexagonal boron nitride: Recent progresses and prospects. Nano Express. 2021 Oct; 2(4):042002. https://doi.org/10.1088/2632-959X/ac2f09
7. Park LS, Oh HS, Lee TH, Kim SH, Hwang JS. Synthesis and thermal properties of poly (phenylene sulfide-co-phenylene sulfide ketone). J Ind Eng Chem. 2000 Sep; 6(5):331-7.
8. Xing J, Deng B, Liu Q. Effect of graphene nanoplatelets on the performance of polyphenylene sulfide composites produced by melt intercalation. High Perform Polym. 2017 Apr; 30(5):519-26. https://doi.org/10.1177/0954008317706733
9. Gu J, Xie C, Li H, Dang J, Geng W, Zhang Q. Thermal percolation behavior of graphene nanoplatelets/polyphenylene sulfide thermal conductivity composites. Polym Compos. 2014 Jun; 35(6):1087-92. https://doi.org/10.1002/pc.22756
10. Kim K, Kim J. Core-shell structured BN/PPS composite film for high thermal conductivity with low filler concentration. Compos Sci Technol. 2016 Oct; 134:209-16. https://doi.org/10.1016/j.compscitech.2016.08.024
11. Ma XK, Lee NH, Oh HJ, Jung SC, Lee WJ, Kim SJ. Morphology control of hexagonal boron nitride by a silane coupling agent. J Cryst Growth. 2011 Feb; 316(1):185-90. https://doi.org/10.1016/j.jcrysgro.2010.12.066
12. Chukov D, Nematulloev S, Zadorozhnyy M, Tcherdyntsev V, Stepashkin A, Zherebtsov D. Structure, mechanical and thermal properties of polyphenylene sulfide and polysulfone impregnated carbon fiber composites. Polymers. 2019 Apr; 11(4):684. https://doi.org/10.3390/polym11040684 PMid:30991729 PMCid:PMC6523300
13. Kubade P, Tambe P. Influence of surface modification of halloysite nanotubes and its localization in PP phase on mechanical and thermal properties of PP/ABS blends. Compos Interfaces. 2017 Sep; 24(5):469-87. https://doi.org/10.1080/09276440.2016.1235442

14. Lohar G, Tambe P, Jogi B. Influence of dual compatibilizer and carbon black on mechanical and thermal properties of PP/ABS blends and their composites. Compos Interfaces. 2020 Feb; 27(12):1101-36. https://doi.org/10.1080/09276440.2020.1726137
15. Hay JN, Luck DA. The conformation of crystalline poly (phenylene sulphide). Polymer. 2001 Sep; 42(19):8297-301. https://doi.org/10.1016/S0032-3861(01)00335-4
16. Goyal RK, Samant SD, Thakar AK, Kadam A. Electrical properties of polymer/expanded graphite nanocomposites with low percolation. J Phys D: Appl Phys. 2010 Aug; 43(36):365404. https://doi.org/10.1088/0022-3727/43/36/365404
17. Khan MO, Leung SN, Chan E, Naguib HE, Dawson F, Adinkrah V. Effects of microsized and nanosized carbon fillers on the thermal and electrical properties of polyphenylene sulfide-based composites. Polym Eng Sci. 2013 Feb; 53(11):2398-406. https://doi.org/10.1002/pen.23503