Received: 2 July 2019 | Revised: 25 November 2019 | Accepted: 1 December 2019

DOI: 10.1002/pc.25479

RESEARCH ARTICLE

Influence of particulate surface treatment on physical, mechanical, thermal, and dielectric behavior of epoxy/hexagonal boron nitride composites

Alok Agrawal[1] | **Saurabh Chandrakar**[2]

[1]Department of Mechanical Engineering, Sagar Institute of Research and Technology Excellence, Bhopal, India

[2]Department of Mechanical Engineering, National Institute of Technology Karnataka, Surathkal, India

Correspondence
Alok Agrawal, Department of Mechanical Engineering, Sagar Institute of Research and Technology Excellence, Bhopal 462041, India.
Email: alokag03@gmail.com

Funding information
Science and Engineering Research Board, Grant/Award Number: ECR/2017/000540

Abstract

Physical, mechanical, thermal, and dielectric behavior of surface modified hexagonal boron nitride (hBN) in epoxy matrix was investigated in this paper. Effective treatment of microsize boron nitride involved silane coupling agent, (γ-aminopropyl)triethoxysilane such that the coating resulted from the treatment amounted to 2% of the weight of silane coupling agent of the treated BN. The present work revealed that the chemical treatment of BN surface could effectively enhance the adhesion between matrix and filler material. The dispersion and wettability of the BN powder in epoxy matrix after surface treatment were improved. These imparted improved physical and excellent mechanical and thermal properties to the developed material. The experimental study on thermal properties of fabricated composites indicated that incorporation of modified particles exhibits improved glass transition temperature. As filler loading increases, coefficient of thermal expansion of composite decreases which further decreases when treated filler were used. Further, appreciable improvement in thermal conductivity is obtained when treated hBN is used in place of untreated one. The dielectric properties are investigated for wide frequency range and filler content and found to be increased with hBN content and decrease with frequency enhancement. Furthermore, mechanical properties of such composites were also largely enhanced when treated fillers were used. With modified properties, the presently developed material is suitable for microelectronic applications.

KEYWORDS

composites, conducting polymers, dielectric properties, mechanical properties, thermal properties

1 | INTRODUCTION

Heat management is one of the most crucial challenges in recent microelectronic technology as power density of electronic devices is rapidly increasing due to miniaturization and integration of such devices.[1] Also, it operates at high frequency and high power condition where large heat flux generated. For better performance of the devices, the efficient removal of accumulated heat is essential to maintain device efficiency and longer lifespan. If not, power leakage, malfunctioning, or even failure of device may take place.[2] Materials used for microelectronic packaging applications need to simultaneously fulfill diverse requirements such as high thermal

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conductivity to dissipate the generated heat effectively and quickly, low coefficient of thermal expansion to avoid thermal fatigue, high glass transition temperature for good dimensional stability, moderate dielectric constant to reduce signal propagation delay, low dielectric loss for better device performance, good moisture absorption resistance, and good mechanical flexibility.[3] Polymeric materials always play an important role in microelectronic applications because of their ease of processing, low cost, low dielectric constant, hydrophobic in nature, and very good adhesive properties.[4] However, common polymers available cannot effectively dissipate the generated heat because they have low thermal conductivity. Also, high coefficient of the thermal expansion of polymer result in thermal failure and low glass transition temperature does not provide thermal stability to it.[5] Hence, increasing the thermal conductivity of polymers while maintaining its dielectric properties opens up large new market. However, the above target can be achieved by incorporating high thermally conducting and electrically insulating ceramic fillers in polymer matrix.

The past work concerning thermal conductive polymer composites are mainly focused on the use of various kinds of fillers such as aluminium nitride (AlN),[5,6] aluminium oxide,[7] boron nitride (BN),[8] $Sm_2Si_2O_7$,[3] magnesium silicate,[4] silicon nitride,[9] and silicon carbide.[10] Apart from single filler reinforcement, the combination of fillers, that is, hybrid fillers were also incorporated to enhance the conductive path. On that note, recently, Pan et al[11] incorporated combination of hexagonal boron nitride (hBN) and AlN of different size in polytetrafluoroethylene polymer and found appreciable enhancement on the conductive behavior of developed material. Similarly, Wang et al[12] used combination of silver and alumina to fabricate epoxy-based composites and reported improvement in the thermal conductivity of epoxy. The key properties of the composite material are dependent on various parameters such as content of filler, number of phases, intrinsic properties of phases, interaction between the filler and matrix, and the method of preparation of composites.[3] Among all, content of filler is mostly considered to be the dominant factor in improving the properties of the filled polymer. By increasing the filler content above 60 wt%, thermal conductivity of polymers improves appreciably. However, increasing the filler content to such higher value results in low strength, low melt flow index, increase in porosity, increase in moisture absorption rate, and have adverse effect on the dielectric properties. Hence, the requirement is to acquire similar thermal conductivity with low content of filler, so that adverse effect of high filler content on polymer composites can be minimize.

For a given filler-matrix combination, the thermal conductivity of the composite can be increased either by maximizing conductive path or by minimizing the thermal contact resistance at the filler-matrix interface. The former is achieved by increasing the amount of conductive filler whereas the latter is achieved by modifying the surface of filler so as to improve interface adhesion between filler and matrix by increasing the affinity between the two. For improvement of interfacial adhesion in the inorganic particulate filled polymer composites, silane coupling agent is generally employed. It is mainly because of its chemical structure. Its peculiarity is that it has two different chemical structures at its two ends. One end on silane coupling agent reacts chemically with polymer and form the bond whereas the other end of coupling agent reacts with the surface of the ceramic filler.[13] On that note, Hou et al[14] studied the thermal and electrical properties of BN when reinforced in epoxy matrix. In their study, they found that inclusion of BN fillers enhances the thermal conductivity of epoxy matrix and reported around 6 to 7 times enhancement when silane coupling agent modified filler were used. They also reported low dielectric permittivity and dielectric loss with high volume resistivity of the developed material over a wide frequency range. More recently, Jia et al[15] used silane modified montmorillonite in epoxy matrix and found that modification of surface of filler material results in low dielectric permittivity, low dielectric loss, and enhanced dielectric strength. Surface modification also influences the thermal properties of the composite by improving the thermal conductivity and stability.

In this study, surface modification of filler is performed so as to improve the affinity between filler and matrix. In particular, silane coupling agent is used for surface treatment of hBN filler. Epoxy is chosen as matrix material in this study. Silane coupling agent acts a bridge to connect the hBN filler and epoxy matrix and thus improves the properties of the composites. The present paper provides the detailed investigation of physical, mechanical, thermal, and dielectric properties of hBN-epoxy composites. The effect of surface treatment of filler and thereby improvement in various physical, mechanical, thermal, and dielectric properties of the composites in view of its application in microelectronic applications were also investigated.

2 | EXPERIMENTAL DETAILS

2.1 | Material considered

Thermoset resin Lapox L12 is used as continuous phase in present investigation. Hardener K6 is commonly employed with Lapox L12 for curing purpose. The matrix

material system selected is supplied by ATUL India Ltd., Gujarat, India. Epoxy used in present investigation possesses density of 1.16 g/cm^3, tensile strength of 40.5 MPa, compressive strength of 85 MPa, and hardness of 0.145 GPa. It has thermal conductivity of 0.212 W/m-K, glass transition temperature of 73°C, CTE of 6.8 × 10^{-5}/°C, and dielectric constant of 4.32 at 1 MHz. BN in its hexagonal crystal structure of size 5 μm used in present investigation is supplied by Souvenier Chemicals, Mumbai. It is of ultrapure grade with purity level of 99%. It has density of 2.3 g/cm^3. It has high thermal conductivity (160-200 W/m-K) for better heat distribution and act as heat sink. It has high thermal stability (CTE = 0.4 × 10^{-5}/°C) to ensure high degree of safety in accidental overheating. It has electrical insulating nature with dielectric constant of 4.8 at frequency of 1 MHz. The silane coupling agent used is supplied by Himedia, India. Its chemical name is (3-aminopropyl) triethoxysilane (APTES) with a molecular weight of 221.37, molecular formula of $C_9H_{23}NO_3Si$ and is supplied by product number RM 6592. It has a shelf life of 4 years and has density of 0.950 g/cm^3.

2.2 | Sample preparation

2.2.1 | Surface treatment of hexagonal boron nitride.

hBN surface treatment using silane coupling agent APTES involved the following steps[10]:

1. A solution of 100 g ethyl alcohol is taken into the flask.
2. 2 g of silane coupling agent APTES is added into ethyl alcohol and stirred for 10 minutes with constant speed to prepare 2 wt% solutions.
3. 100 g hBN is added into the ethyl alcohol/APTES solution and stirred for another 20 minutes with constant speed.
4. Heating the mixture at 80°C and refluxing for 2 hours and then cooling at room temperature while stirring.
5. Rinsing the mixture with alcohol by filtration.
6. The solid recovered was dried in oven at 100°C for 12 hours to obtain APTES modified hBN.

2.2.2 | Fabrication of epoxy/hBN composites

In the present investigation, hBN filled epoxy composite is fabricated using simple hand lay-up technique. The resin (L-12) and hardener (K-6) are combined in 10:1 ratio by weight as per the instruction of the supplier. hBN in its untreated form and treated from is added separately to the combination which is mixed manually. Thin coating of silicon spray is performed over mold before pouring the mixture in the mold, so that it will easy to remove the composite once it gets cured. The cast is then pressed using compression molding machine at a pressure of 1 kgf to remove the trapped air bubbles to the maximum extent. It is then cured for 12 hours and then taken out carefully from the mold. Composites were fabricated with different weight fraction of filler. The list of fabricated composite is presented in Table 1.

2.3 | Characterization

The density of fabricated composites was measured by well-known Archimedes method (ASTM D 792-91). Rule of mixture model is used to predict the theoretical density (ρ_t) of composite for varied weight fractions for filler. The void content (V_v) in composites is evaluated with measured and calculated density. Water absorption behavior of hBN filled epoxy composite was experimented as per ASTM D 570. To study the rate of water absorption, the samples of same surface area were submerged in distilled water. The samples were periodically taken out and immediately weighted and the percentage difference in the gain of weight defines the water absorption behavior. The tensile and compressive strength is measured using computerized Tinius Olsen universal testing machine in accordance with ASTM D638 and ASTM D695, respectively. Brinell hardness test was carried out in accordance

TABLE 1 List of epoxy/hBN fabricated samples

Set	Composition	Set	Composition
A1	Epoxy +5 wt of raw hBN	B1	Epoxy +5 wt% of surface modified hBN
A2	Epoxy +10 wt% of raw hBN	B2	Epoxy +10 wt% of surface modified hBN
A3	Epoxy +15 wt% of raw hBN	B3	Epoxy +15 wt% of surface modified hBN
A4	Epoxy +20 wt% of raw hBN	B4	Epoxy +20 wt% of surface modified hBN
A5	Epoxy +25 wt% of raw hBN	B5	Epoxy +25 wt% of surface modified hBN
A6	Epoxy +30 wt% of raw hBN	B6	Epoxy +30 wt% of surface modified hBN
A7	Epoxy +35 wt% of raw hBN	B7	Epoxy +35 wt% of surface modified hBN
A8	Epoxy +40 wt% of raw hBN	B8	Epoxy +40 wt% of surface modified hBN

with ASTM E-10 using Affri LD250 hardness measuring instrument. Unitherm Model 2022 is used to measure thermal conductivity in accordance with ASTM E-1530. Coefficient of thermal expansion and glass transition temperature were measured using Perkin-Elmer thermal mechanical analyzer (TMA-7) following standard ASTM D 618 and ASTM E 831, respectively. Dielectric constants were measured with Hioki 3532-50 Hi Tester LCR analyzer between 1 kHz and 1 GHz frequency range.

3 | RESULTS AND DISCUSSION

3.1 | Density and void content

The density of epoxy is measured using Archimedes method and found to be 1.16 g/cm^3. The same method is implemented for evaluating the density of the fabricated composites. Figure 1A shows the measured and calculated density of the epoxy/hBN composites with varying content of raw and surface modified hBN filler. As the intrinsic density of hBN is more than epoxy, its incorporation in epoxy increases the density of composite which can be clearly seen in the figure. Again, the density is more for epoxy/hBN composites with treated filler as compared to that with untreated filler. This shows the good adhesion between the filler and matrix phase when surface modified filler were used. The theoretical density is calculated using rule of mixture model considering epoxy density as 1.16 g/cm^3 and hBN density as 2.3 g/cm^3. Again, it was considered that modification of hBN surface not altered density of hBN, so the calculated density for both sets of composites remains same. From the measured and calculated density, it was found that there is maximum deviation of around 4% and 8% for hBN/epoxy composites with and without surface modified hBN. This deviation is primarily due because of voids present inside the composites which increases with hBN content as we consider that composite consist of three phases, that is, matrix, filler, and voids. The porosity was calculated and values obtained were shown in Figure 1B. It is observed from figure that with increase in hBN content, percentage of void also increases for both sets of composites. However, the epoxy composites with treated filler show lower porosity value when compared with that of epoxy composites with untreated filler. This is a pure evidence for the strong adhesion between the epoxy matrix and surface modified hBN filler. For set A composites, maximum porosity value obtained is 8.07% whereas for set B composites exhibits a percentage porosity of 3.93% at 40 wt% of filler loading.

3.2 | Water absorption behavior

Moisture absorption in composite has significant influence on degradation of different properties of the composites. Absorbed water cause swelling in matrix and result in formation of cracks reduces mechanical strength, thermal conductivity, glass transition temperature, and alter the dielectric properties. Figure 2 shows the water absorption rate of all the fabricated composites

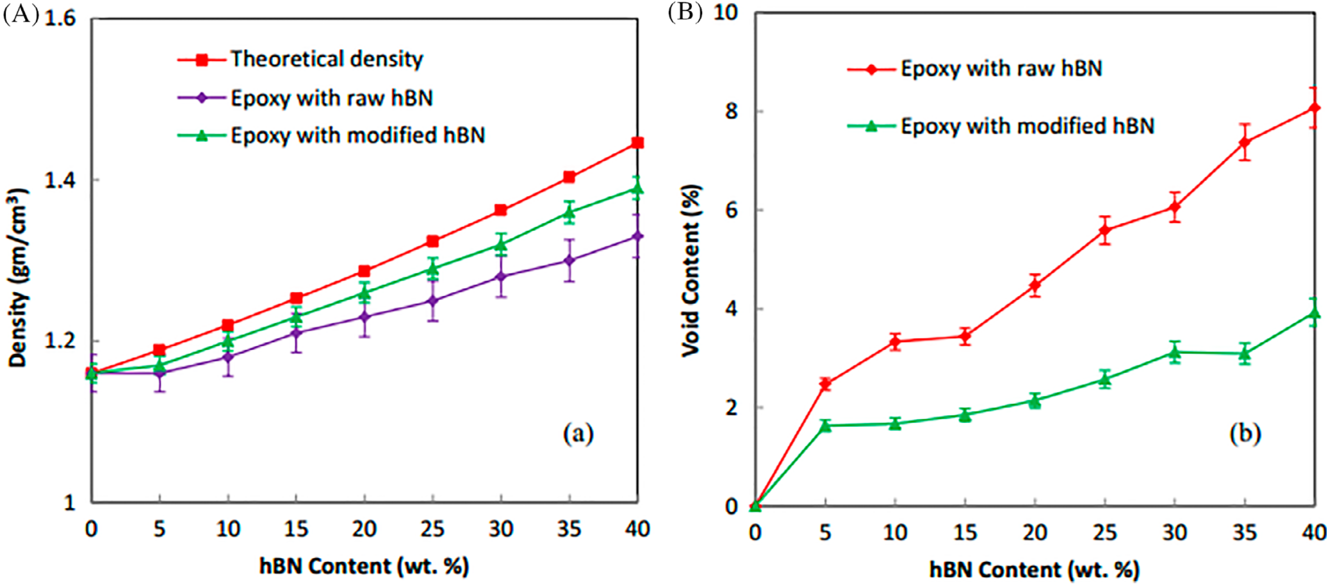

FIGURE 1 (A) Theoretical and measured density and (B) void content of epoxy/hBN composites [Color figure can be viewed at wileyonlinelibrary.com]

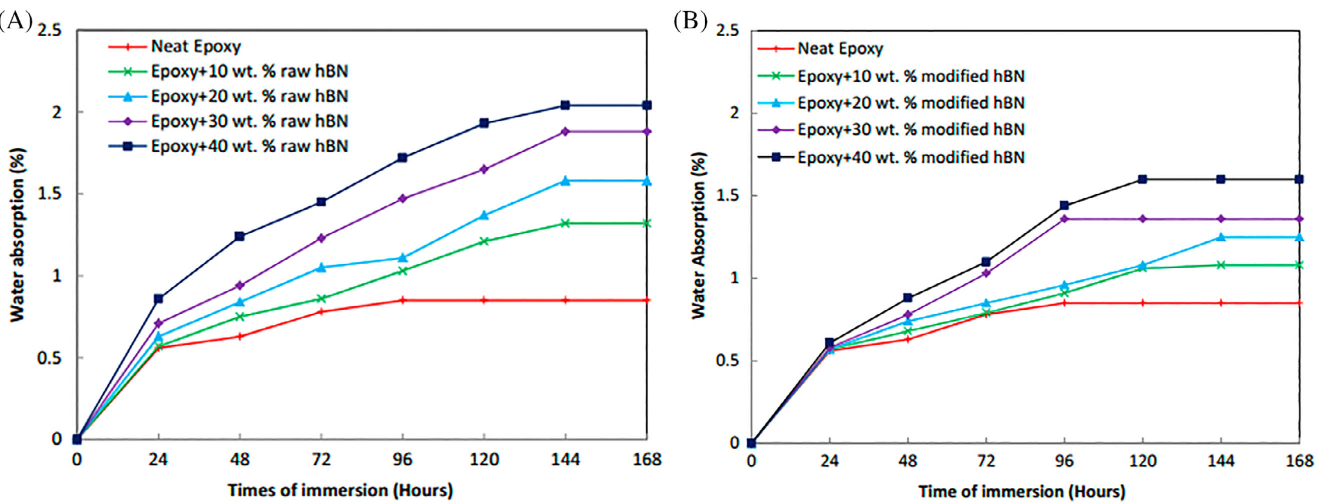

FIGURE 2 Water absorption rates of epoxy/hBN composites with (A) raw hBN and (B) modified hBN [Color figure can be viewed at wileyonlinelibrary.com]

under investigation. The composite specimens were dried in the hot air oven at 75°C for 4 hours until they reach constant weight and then immersed in the water. Specimens are taken out from distilled water at regular period of time, that is, after every 24 hour. The molecules of water that is adhered with the specimen surface are dried using cotton cloth and weighted again. The complete process of removal of sample from water and weighing is performed in short time, so that no desorption of water may take place. The experiments were performed for duration till the saturation stage in water absorption reached. From the figures, it is clear that epoxy filled with hBN has higher rate of water absorption as compared to neat epoxy resin. Also, this water absorption rate increases with increase in hBN content in epoxy resin. It is mainly because of more number of entrapped voids present in the composites with increase in hBN content. Maximum water absorption is around 2% for filler loading of 40 wt% for a span of 168 hours. Composites developed from surface modified hBN particles have relatively less water absorption as compared to raw hBN particles for similar loading. Maximum water absorption is around 1.5% for filler loading of 40 wt% for similar duration. The improvement is subjected to improved interaction and chemical affection between filler and matrix which reduces the tendency to absorb moisture. From the figure, it is seen that water absorbed by the composite is linear in nature initially. Then, absorption reduces and slopes of the curve decreases. Later, it increases again mainly because of degradation of continuous phase which give rise to penetration of moisture through the microcracks generated due to the presence of voids. Almost similar trends were observed by Nayak et al[16] in their work. It is further observed that for neat epoxy, saturation in water absorption occurs around 72 hours whereas for its composites, it saturation attains at 144 hours for Set A composites whereas for Set B composites, saturation occurs much earlier that is, at around 120 hours. This is due to less microcracks generated in Set B composites compared to set A composites due to the less voids present.

3.3 | Tensile strength

Tensile strength of composite depends mainly on the stress transfer efficiency across the interface. The dependence of tensile strength of epoxy composites filled hBN (raw and surface modified hBN) with different content is shown in Figure 3. The tensile strength of epoxy/hBN composites increased with hBN content when hBN content is upto 10 wt%. The ultimate tensile strength of unfilled epoxy is measured to be 40.5 MPa which increases to 44.6 and 45.2 MPa at a loading of 10 wt% of raw and modified hBN, respectively. However, when hBN content increases beyond 10 wt%, tensile strength of the composite decrease. For maximum filler loading of 40 wt%, the tensile strength of composites decreased to 18.2 and 30.8 MPa. Similar trend was obtained for flexural strength of composites.[9,17] A limited quantity of filler can successfully remedy the defects form epoxy self-curing. Meanwhile, BN can transfer stress and avoid the expanding of cracks, thus enhancing tensile strength. The drastic decline in tensile strength, as a result of high loading of hBN, may be clarified by the fact that excessive fillers served as local stress-concentration points in the resin matrix. With certain level increment of hBN content, one of the physical properties, that is, viscosity of

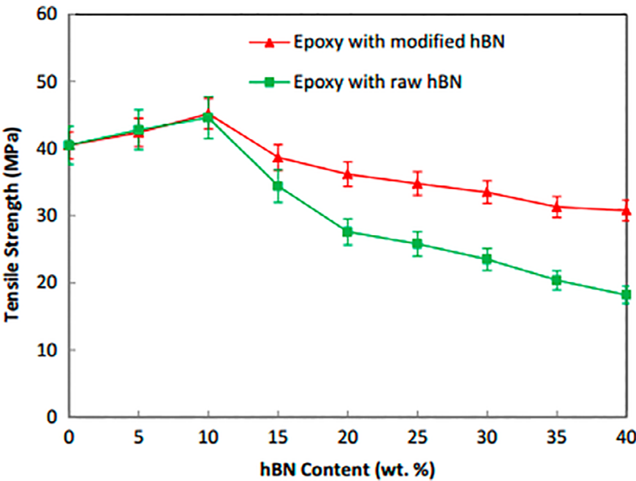

FIGURE 3 Tensile strength of epoxy/hBN composites with raw hBN and modified hBN [Color figure can be viewed at wileyonlinelibrary.com]

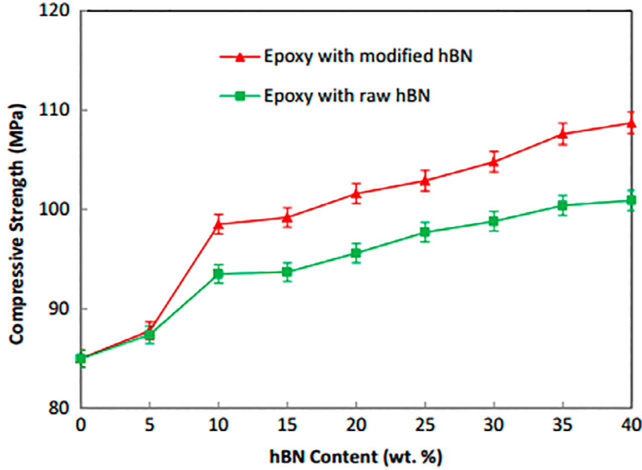

FIGURE 4 Compressive strength of epoxy/hBN composites with raw hBN and modified hBN [Color figure can be viewed at wileyonlinelibrary.com]

the combination began to intensify quickly due to the nonappearance of inertia solvent such as acetone.[18] Consequently, presence of interfacial defects, pitiable wettability between the two phases might generated in the composites, causing in the weakening in tensile strength. Further, it can be seen that when modified hBN were incorporated in epoxy matrix, the decreasing trend in tensile strength exist, but the rate of decrement decreases appreciably. This improvement in tensile strength mainly attributed to the more uniform dispersion and improved adhesion between the epoxy and hBN originates.

3.4 | Compressive strength

The dependence of compressive strength of epoxy composites filled with hBN (raw and surface modified) with different filler content is shown in Figure 4. It can be seen that with increase in hBN content, compressive strength of the composites increases, irrespective of the untreated or treated hBN. With raw hBN in epoxy matrix, compressive strength increases from 85 MPa for neat epoxy to 100.9 MPa for 40 wt% hBN in epoxy. This is an increment of 18.7%. The main reason of such improvement is high compressive strength of hBN particles. Further, favorable deformation processes facilitated by the presence of fillers in the matrix result in compressive strength improvement. Also, in a compression test, voids present get closed when load is applied contrary to tensile loading situation where voids get open up result in quick generation of cracks.[19] Also, the increment in compressive strength is more for treated hBN. In this case, compressive strength increases to 108.7 MPa for 40 wt% modified hBN which is an increment of 27.9% which is again resulted from good dispersion and compatibility between both the phases.

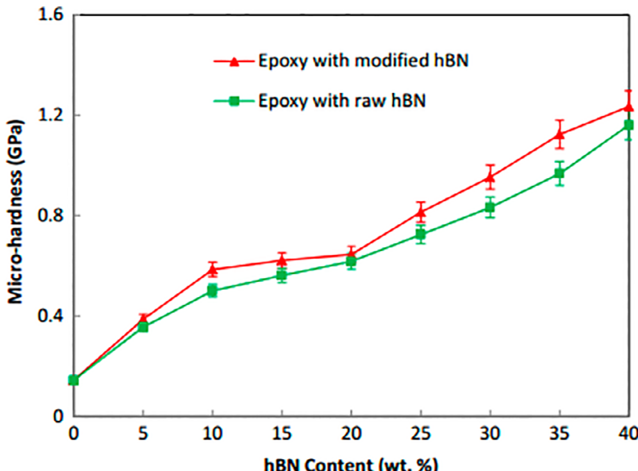

FIGURE 5 Microhardness of epoxy/hBN composites with raw hBN and modified hBN [Color figure can be viewed at wileyonlinelibrary.com]

3.5 | Microhardness

The dependence of microhardness of epoxy composites filled with hBN (raw and surface modified) with different filler content is shown in Figure 5. As the hardness of hBN is more as compared to epoxy resin, its incorporation in epoxy results in increase in its microhardness value. Modulus of the particulate filled polymer

composite increased with filler content leading to a corresponding increase in the hardness of the composite. For 40 wt% hBN content hardness increases from 0.145 to 1.161 GPa for Set A composites which is around eight times that of neat epoxy. The increment in hardness increases further when the surface modified hBN is used in epoxy and reaches maximum to 1.235 GPa for set B composites for filler content of 40 wt%. The composite with raw hBN has higher porosity and higher moisture absorption which affects the overall strength of composites.

3.6 | Thermal conductivity

The thermal conductivity value of epoxy matrix and its microcomposites at various level of hBN loading are shown in Figure 6. The epoxy used in present work has a very low thermal conductivity of 0.211 W/m-K and by adding the hBN, the thermal conductivity nonlinearly increases with increasing hBN content. This phenomenon can be explained by the dependence of thermal conductivity of the composites on the content of conductive filler. When the conductive filler content was low in matrix, the filler was randomly distributed in matrix with no contact among themselves. When the content of filler increased continuously, the filler could come in contact and form the thermally conductive path within the matrix body, leading to the higher thermal conductivity. It can be seen from the figure that for low filler content, rate of increase of thermal conductivity is low, whereas when filler content increased beyond 30 wt%, increment rate increases. When the loading of raw hBN was 40 wt%, the thermal conductivity of the composite reached 1.31 W/m-K. The improvement is of around 518% than that of neat epoxy. When the modified hBN content was 40 wt% in epoxy, the thermal conductivity was increased to 1.52 W/m-K which is an increment of around 617%. From the analysis, it can be found that the silane modified hBN exhibit higher thermal conductivity than unmodified hBN for same filler loading. It is very well known that composite body is multiphase system. In the present case, we used one matrix material and one filler material, so the system is two-phase system. In such system, interfacial status is very significant for thermal conductivity. It is because phonon-scattering processes which are responsible for thermal conduction or resistance becomes very sensitive to interfacial defects. If there are flaws associated with the matrix-filler interface, it acts as thermal barrier and restrict the transmission of heat.

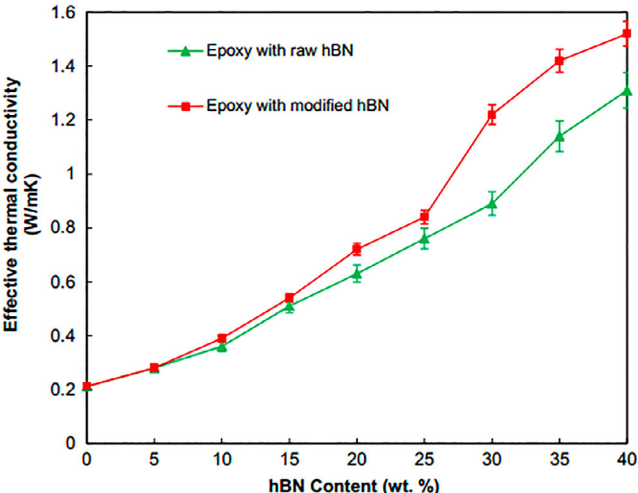

FIGURE 6 Thermal conductivity of epoxy/hBN composites with raw hBN and modified hBN [Color figure can be viewed at wileyonlinelibrary.com]

Silane modification of hBN improves both dispersion and interfacial interaction of filler in and with matrix, respectively. Actually, silane molecule acts as a bridge between filler and matrix which lower the thermal resistance barrier between epoxy resin and hBN particles resulting in increased thermal conductivity. Also with modified filler, void content in the composite body reduces significantly and the thermal conductivity of air voids is very low, that is, around 0.0024 W/mK which is another factor of increment of thermal conductivity. In past research, Wu et al[20] reported similar trend in the variation of thermal conductivity for AlN reinforced in polyethermide composite. They reported increment of 733% in conductivity of matrix with 57.4 vol% of modified AlN filler against increment of 504% with same content of unmodified AlN filler.

3.7 | Glass transition temperature

Glass transition temperature of different composites specimen developed in present study is shown in Figure 7. It is an important property of polymer, as at this temperature polymer changes its behavior from glassy state to rubbery state. It can be seen from the figure that glass transition temperature of epoxy composites was higher as compared to that of neat epoxy and it increases with increase in hBN content. With raw hBN, glass transition temperature increases from 73°C for neat epoxy to 87.1°C for 40 wt% filled epoxy. Further with silane modified hBN, glass transition temperature increases to 93.2°C with similar filler content. Glass transition temperature of thermoset polymer depends upon various factors which includes free volume of polymer, interaction between filler and matrix, density of cross linking, and

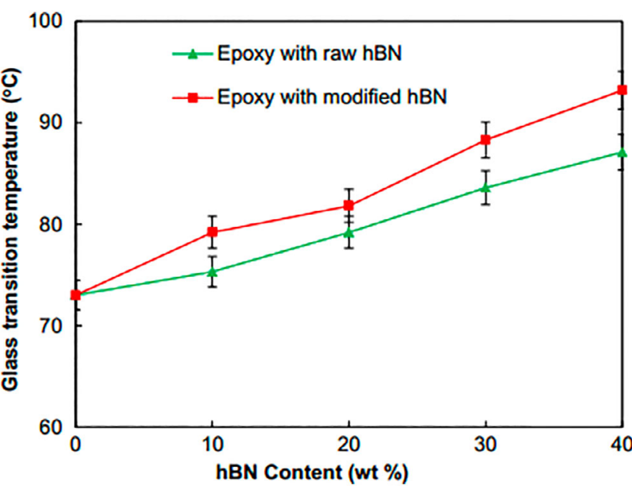

FIGURE 7 Glass transition temperatures of epoxy/hBN composites with raw hBN and modified hBN [Color figure can be viewed at wileyonlinelibrary.com]

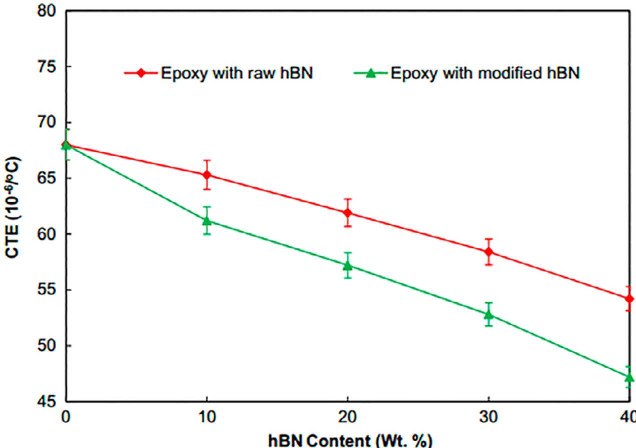

FIGURE 8 Coefficient of thermal expansion of epoxy/hBN composites with raw hBN and modified hBN [Color figure can be viewed at wileyonlinelibrary.com]

cure schedule. In this study, change in free volume and interaction between filler and matrix are considered to be the governing factors for glass transition temperature as rest of the parameter remains constant for each set of composite as we are not changing the processing technique. Increase in glass transition temperature with increase in filler content is mainly due to decrement in free volume which is otherwise present in polymer matrix. This decrement in free volume restricts the mobility of polymer chain which increases the glass transition temperature.[21] Also, glass transition temperature further increased when silane modified hBN is used in epoxy matrix which is mainly because of better interaction between filler and matrix. Silane acts as a bridge between matrix and filler phase which improve the affinity between filler and matrix leading to the enhanced interaction between the phases. Similar trend was obtained by Wu et al[20] in their study on AlN/polyethermide composite.

3.8 | Coefficient of thermal expansion

The variations in coefficient of thermal expansion of epoxy/hBN composites with filler content for composites prepared using both raw and treated hBN are shown in Figure 8. Addition of hBN particles into epoxy matrix results in a decrement in the value of CTE. It is mainly because of the constrained mobility arises in the molecules of polymers due to adsorption of hBN surfaces. Also, CTE of hBN filler is very low as compared to CTE of neat epoxy. The CTE of the composite reduces from $6.8 \times 10^{-5}/^{o}C$ to $5.42 \times 10^{-5}/^{o}C$ for epoxy-based composite incorporated with 40 wt% of raw hBN. The decrement in the value of CTE is gradual with increase in filler content, as the distance between the particle decreases with increase in filler content and because of that, there is a transition from loosely bound polymer to tightly bound polymer over the particle surface. With this, constrained grows within the composite body and suppresses the expansion of polymer-filler combination. The CTE of the composite reduces from $6.8 \times 10^{-5}/^{o}C$ to $4.72 \times 10^{-5}/^{o}C$ for epoxy-based composite incorporated with 40 wt% of silane treated hBN. It can be seen that there is additional decrement in CTE when modified hBN is used. It is mainly because of the two reasons: (a) modification of filler improves the dispersion of particles in the matrix body and (b) adhesion between the filler and matrix increases when modified hBN is used.[4] With good dispersion and adhesion of filler in and within matrix, it restricts the movement of polymer chain and significantly reduces the expansion phenomenon of polymer chain.

3.9 | Dielectric constant

In electronic packaging application, the dielectric constant of the materials is vital. To achieve faster speed and less attenuation of signal transmission in high frequency, the material with low dielectric constant is preferable. The frequency dependence of dielectric constant of material is important factor which predict its overall performance. The dielectric constant of hBN/epoxy composites as a function of frequency for different weight fraction of filler is shown in Figure 9. It is seen from the figure that dielectric constant of composite increases with increase in filler content. However, the dielectric constant of both

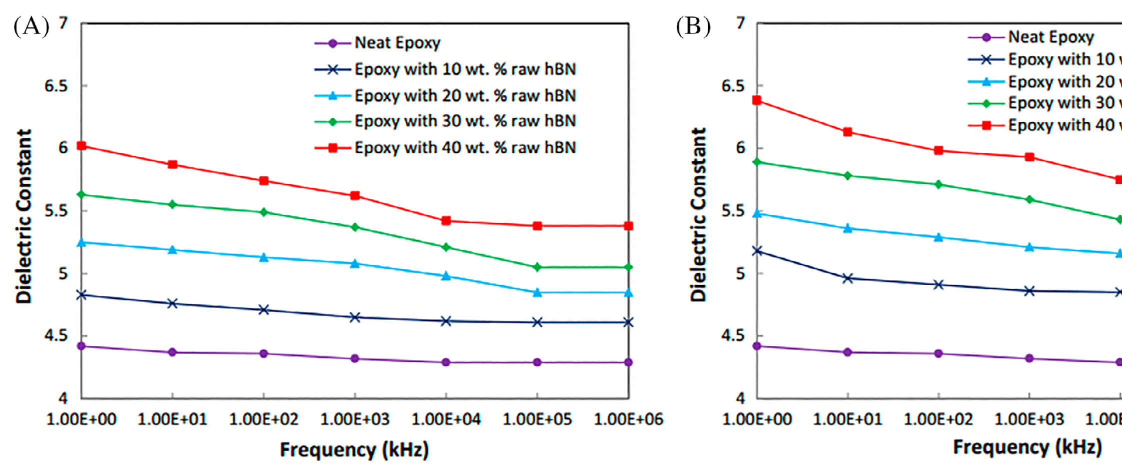

FIGURE 9 Dielectric constant of epoxy/hBN composites (A) raw hBN and (B) modified hBN [Color figure can be viewed at wileyonlinelibrary.com]

epoxy and hBN are low but their composite exhibits higher dielectric constant than individual. Dielectric constant of epoxy with 40 wt% raw hBN 5.62 at 1 MHz and 5.38 at 1 GHz whereas, with 40 wt% modified hBN in epoxy, dielectric constant is 5.93 at 1 MHz and 5.71 at 1 GHz. It is mainly because of the existence of certain polar group such as hydroxyl and amino on the edge surface of hBN. Both the polar groups have high electrical conductivity and with hBN incorporation in epoxy increase, number of polar group increase which increases the dielectric constant of the composites. Similar trend was obtained by Pan et al[22] during their investigation on hBN in the form of platelets with PTFE powder. It is observed that dielectric constant further increases with filler content when modified hBN is incorporated in epoxy. The air voids have very low dielectric constant and are present in more quantity when raw hBN was used. With modified hBN, air voids reduced appreciably and because of that, dielectric constant is more for modified hBN for same filler content than that for raw hBN.

Figure also presents the variation of dielectric constant of epoxy/hBN composites as a function of frequency. It can be seen that dielectric constant of pure epoxy have good frequency stability as there is marginal change in its value over a wide range of frequency. Frequency dependence originates when hBN is added in epoxy and increase with increase in hBN content. The dielectric constant of the composites decreases with increase in frequency. In neat polymer, only dipolar polarization exists and therefore reduction in dielectric constant with increase in frequency is minimal. However, when filler is added in matrix, it makes the whole system heterogeneous because apart from filler, certain impurities may also unknowingly enter the system during fabrication. This results in growth of interfacial polarization and because of it, charge carrier originates at the interface. The decrease in the dielectric constant with an increase in frequency is due to the reason that the interfacial dipoles have less time to orient themselves in the direction of the alternating electric field.[6]

4 | CONCLUSIONS

The effect of hBN microparticulate on physical, mechanical, thermal, and dielectric properties of epoxy-based composites is investigated. The influence of surface modification of filler particles with silane coupling agent on different properties was also reported. From the analysis, it was found that modified hBN possess good dispersion and wettability in the epoxy matrix and thus improve the adhesion between them. With modified hBN, porosity and water absorption rate of composites reduced significantly even for high filler loading. With reduced porosity, mechanical and thermal properties of the composites improved. Tensile strength of the composites increased from 40.5 to 45.2 MPa with 10 wt. of hBN which reduces with further increase of filler but remain on higher end as compared to when raw hBN is added in epoxy. With raw and modified hBN in epoxy matrix, compressive strength increases to 100.9 and 108.7 MPa, respectively, for 40 wt% hBN. Microhardness increases from 0.145 to 1.161 GPa with raw hBN and 1.235 GPa with modified hBN for similar filler loading. For maximum filler loading of 40 wt%, thermal conductivity increases from 0.212 W/mK (neat epoxy) to 1.31 W/mK (with raw hBN) and 1.52 W/mK (with modified hBN), glass transition temperature increases from 73°C (neat epoxy) to 87.1°C (with raw hBN) and 93.2°C (with modified hBN) whereas CTE decreases from $68 \times 10^{-6}/^{o}C$ (neat epoxy) to

$54.2 \times 10^{-6}/^{o}C$ (with raw hBN) and $47.2 \times 10^{-6}/^{o}C$ (with modified hBN). The composites with modified hBN particulates exhibit higher dielectric constant than untreated filler mainly because of low porosity in former as dielectric constant of air is very less as compared to either of the phase present in composites.

ACKNOWLEDGMENTS

This work was financial supported by Science and Engineering Research Board, India (Grant numbers ECR/2017/000540).

ORCID

Alok Agrawal https://orcid.org/0000-0002-2760-1880
Saurabh Chandrakar https://orcid.org/0000-0002-0979-6653

REFERENCES

[1] H. Fang, S. L. Bai, C. P. Wong, *Composites, Part A* **2017**, *100*, 71.
[2] Y. K. Kim, J. Y. Chung, J. G. Lee, Y. K. Baek, P. W. Shin, *Composites, Part A* **2017**, *98*, 184.
[3] S. Thomas, V. Deepu, S. Uma, P. Mohanan, J. Philip, M. T. Sebastian, *Mater. Sci. Eng. B* **2009**, *163*, 67.
[4] T. S. Sasikala, M. T. Sebastian, *Ceram. Int.* **2016**, *42*, 7551.
[5] C. Pan, K. Kou, G. Wu, Y. Zhang, Y. Wang, *J. Mater. Sci.: Mater. Electron.* **2016**, *27*, 286.
[6] A. Agrawal, A. Satapathy, *Composites, Part A* **2014**, *63*, 51.
[7] A. Agrawal, A. Satapathy, *Polym. Compos.* **2015**, *36*, 102.
[8] J. Hou, G. Li, N. Yang, L. Qin, M. E. Grami, Q. Zhang, N. Wang, X. Qu, *RSC Advan.* **2014**, *4*, 44282.
[9] N. Ramdani, M. Derradji, T. T. Feng, Z. Tong, J. Wang, E. O. Mokhnache, W. B. Liu, *Mater. Lett.* **2015**, *155*, 34.
[10] W. Zhou, D. Yu, C. Min, Y. Fu, X. Guo, *J. Appl. Polym. Sci.* **2009**, *112*, 1695.
[11] C. Pan, K. Kou, Y. Zhang, Z. Li, G. Wu, *Composites, Part B* **2018**, *153*, 1.
[12] Z. Wang, M. Yang, Y. Cheng, J. Liu, B. Xioa, S. Chen, J. Huang, Q. Xie, G. Wu, H. Wu, *Composites, Part A* **2019**, *118*, 302.
[13] Y. Xu, D. D. L. Chung, *Compos. Interfaces* **2000**, *7*, 243.
[14] W. Zhou, J. Zuo, X. Zhang, A. Zhou, *J. Compos. Mater.* **2014**, *48*, 2517.
[15] Z. R. Jia, Z. G. Gao, D. Lan, Y. H. Cheng, G. L. Wu, H. J. Wu, *Chinese Physics B* **2018**, *27*, 117806.
[16] R. K. Nayak, K. K. Mahato, B. C. Ray, *Composites, Part A* **2016**, *90*, 736.
[17] J. Gu, Q. Zhang, J. Dang, C. Xie, *Polym. Adv. Technol.* **2012**, *23*, 1025.
[18] W. Zhou, S. Qi, T. Ai, H. Zhao, M. Zhang, W. Li, E. Lau, *J. Appl. Polym. Sci.* **2009**, *111*, 255.
[19] A. Agrawal, A. Satapathy, *Polym. Compos.* **2019**, *40*, 2573. https://doi.org/10.1002/pc.25050.
[20] S. Y. Wu, Y. L. Huang, C. C. M. Ma, S. M. Yuen, C. C. Teng, S. Y. Yang, *Composites, Part A* **2011**, *42*, 1573.
[21] K. C. Yung, B. L. Zhu, T. M. Yue, C. S. Xie, *Compos. Sci. Technol.* **2009**, *69*, 260.
[22] C. Pan, J. Zhang, K. Kou, Y. Zhang, G. Wu, *Int. J. Heat Mass Transfer* **2018**, *120*, 1.

How to cite this article: Agrawal A, Chandrakar S. Influence of particulate surface treatment on physical, mechanical, thermal, and dielectric behavior of epoxy/hexagonal boron nitride composites. *Polymer Composites*. 2019;1–10. https://doi.org/10.1002/pc.25479